Electronic Interpretation of Organic Reaction Mechanism. VII. Reactions and Structures of Organic Halides in Replacement Reactions

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Many of the previous workers who have studied on the SN2 type reactions indicate that the following compounds show extremely high reactivities toward nucleophilic reagents:

$CH_2=CH-CH_2-Cl$, $PhCH_2-Cl$,

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-Cl$, $Ph-\overset{O}{\overset{\|}{C}}-CH_2-Cl$,

$C_2H_5O-\overset{O}{\overset{\|}{C}}-CH_2-Cl$.[1]

In order to study why these compounds are highly reactive in the SN2 type reactions, an experiment was made by the present authors using the reaction of ionization mechanism (Pull type). For this type of reaction, the organic halides were interacted on silver nitrate in absolute alcohol. As the previous workers[2] have reported that silver nitrates react with alkyl halide by the ionization mechanism (Pull type) and that it exerts too much catalytic activities in the reaction, the same state was recognized also by the authors. However, since it was found that this catalytic action depended chiefly on the sensitized silver chloride, our experiments with silver nitrate were carried out in a dark room in order to avoid the irregular catalytic action. Our experiments show that allyl chloride and benzyl chloride are much more reactive than the ordinary normal alkyl chloride but that chloroacetone, ω-chloroacetophenone and ethyl chloroacetate do not react so easily as n-butyl chloride does.

In order to find the effect produced by the second or third chlorine atom of these compounds which have two or three chlorine atoms on the same carbon, the authors made the experiments of the reactions of the polychlorides of n-butane and of those of α-polychloroderivatives of toluene with silver nitrate and with potassium iodide. The results indicate that n-butylidene chloride is less reactive than n-butyl chloride in both reactions, *i.e.* with silver nitrate and with potassium iodide, while in the series of benzyl chloride, the reactivities decrease with the increase in number of chlorine atoms on the same carbon atom in the case with potassium iodide and increase with the increase in number of chlorine atoms in the case with silver nitrate.

Experimental

Experimental Procedure:—The temperature of the thermostat used for this kinetic measurements was held within 0.1°. The method of determination used in the reaction with silver nitrate was similar to that used by Burke and Donnan[2a] except the fact that our experiments were performed in sealed tubes in a dark room. A mixture of 5 cc. each of 2 N alcoholic solutions of organic chloride and silver nitrate was sealed in a 20 cc. test tube and the test tube was immersed in the thermostat as quickly as possible. At regular intervals, the sealed tube was broken and the content was washed into 25 cc. of 0.05 N solution of NH_4SCN and then this mixture was back titrated with 0.2 N silver nitrate using iron alum as an indicater. To avoid large catalytic activities produced by silver chloride formed, the reaction was stopped when 30% of the organic chloride had reacted. The velocity constants were obtained from the following equation:

$$k=\frac{1}{t}\left(\frac{1}{C}-\frac{1}{C_0}\right) \qquad (i)$$

where C is the concentration of silver nitrate at time t, while C_0 is the initial concentration of silver nitrate.

For the reaction with potassium iodide in acetone, the authors followed the method described by Conant and his co-workers.[1a] Since this method has been used quite extensively, it is not described here.

Materials:—The solvent used was absolute alcohol which was prepared by boiling dry alcohol with silver nitrate for a few hours. The solution of silver nitrate can be kept in dark without

(1) (a) Conant, Kirner and Hussey, *J. Am. Chem. Soc.*, **66**, 232 (1924); **47**, 478, 488 (1925).
(b) Clarke, *J. Chem. Soc.*, **97**, 416 (1916).
(c) Wilson, *Chem. Rev.*, **16**, 149 (1935).
(2) (a) Burke and Donnan, *J. Chem. Soc.*, **85**, 555 (1904).
(b) Senter, *J. Chem. Soc.*, **97**, 346 (1916).
(c) Hammett. "Physical Organic Chemistry" Chapter V.

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spoiling for a week, but the authors avoided to use the solution which was prepared more than a week before the experiment. At each time the solution was freshly prepared.

Both allyl chloride and benzyl chloride used were the commercial products. *n*-Butylidene chloride and benzal chloride were prepared from the corresponding aldehyde by reacting these with phosphor pentachloride. Benzotrichloride was prepared by the reaction of benzyl chloride with chlorine. Monochloroacetone and ω-chloroacetophenone were prepared by reacting the corresponding ketone with chlorine, *n*-butyl chloride from *n*-butyl alcohol and hydrochloric acid using zinc chloride as a catalyst, and ethyl chloroacetate by the ordinary esterification of chloroacetic acid with ethanol. All these compounds were washed with dilute sodium carbonate solution, dried over calcium chloride and then distilled for sometimes. The boiling points of these compounds are as follows:

$CH_2=CH-CH_2-Cl$	45°
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-Cl$	119°
$Ph-CH_2-Cl$	179°
$CH_3-CH_2-CH_2-CH_2-Cl$	77.5°
$C_2H_5O-\overset{O}{\overset{\|}{C}}-CH_2-Cl$	143-4°
$Ph-CHCl_2$	88-9° (14 mm.)
$CH_3-CH_2-CH_2CHCl_2$	114-5°
$Ph-\overset{O}{\overset{\|}{C}}-CH_2Cl$	m. p. 56°
$Ph-CCl_3$	104-5° (25 mm.).

Products were investigated in the case of benzyl chloride. Seventeen g. of silver nitrate and 12 g. of benzyl chloride were reacted in 500 cc. absolute alcohol. After filtering the silver chloride precipitated, alcohol was removed by evaporation, thereby leaving some oily substance. Main parts of this oil (15 g.) distilled over at 95–106° under a reduced pressure of 19 mm. This oil gave a deep violet color when treated with diphenylamine and conc. sullfuric acid, which indicated the presence of $-NO_3$ group in the molecule. When this oil was treated with caustic soda, benzaldehyde and benzoic acid were obtained. Benzaldehyde was comfirmed by converting it to 2, 4-dinitrophenylhydrazone, which melted at 131°, and did not show any fall of its melting point when it was mixed with the known sample. Benzoic acid was confirmed by its melting point and mixed melting point with the known. These experiments indicated that the product obtained in this experiment was benzyl nitrate.

Results

The bimolecular velocity constants obtained by the reaction with silver nitrate of *n*-butyl chloride, allyl chloride, benzyl chloride, chloroacetone, ω-chloroacetophenone and ethyl chloroacetate are given in Table 1.

Table 1

Bimolecular Velocity Constants in the Reaction of Organic Chloride with Silver Nitrate in Absolute Alcohol at 50°

Compounds	10^{-5} k at 50°C, l., mol.$^{-1}$ min.$^{-1}$
$CH_3-CH_2-CH_2-CH_2-Cl$	1.2
$CH_2=CH-CH_2-Cl$	7.9
$Ph-CH_2-Cl$	83.0
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-Cl$	0.31
$Ph-\overset{O}{\overset{\|}{C}}-CH_2-Cl$	0.67
$C_2H_5O-\overset{O}{\overset{\|}{C}}-CH_2-Cl$	0.32

Bimolecular velocity constants of the reaction with silver nitrate for *n*-butylidene chloride, *n*-butyl chloride, benzyl chloride, benzal chloride, and benzotrichloride are summarized in Table 2.

Table 2

Bimolecular Velocity Constants of the Reaction of Organic Polychlorides with Silver Nitrate in Absolute Alcohol

Compounds	Temp. °C	10^{-5} k, l., mol.$^{-1}$ min.$^{-1}$
$CH_3-CH_2-CH_2-CH_2-Cl$	50	1.2
$CH_3-CH_2-CH_2-CHCl_2$	50	0.13*
$Ph-CH_2-Cl$	20	8.4
$Ph-CHCl_2$	20	76.7*
$Ph-CCl_3$	20	102.5*

In the case of polychlorides (these with asterisk in Table 2) the observed values of k obtained from the equation (1) were divided by the number of chlorine atome present in the molecule in order to get the velocity constants of the splitting of the first chlorine at the initial step of this reaction; therefore the values with asterisk are all treated accordingly. The reason is that the second and the third step of this reaction are very fast as compared to the first.

In Table 3, the velocity constants of polychlorides in the reaction with potassium iodide are summarized.

In order to observe the action of silver chloride formed and of sensitized silver chloride, the reactivities in the following three cases were compared: (a) the ordinary reaction between

Table 3

Bimolecular Velocity Constants of Polychlorides in the Reaction with Potassium Iodide in Absolute Acetone

Compounds	Temperature, °C.	k
$CH_3—CH_2—CH_2—CH_2—Cl$	60	0.12
$CH_3—CH_2—CH_2—CHCl_2$	60	0.00
$Ph—CH_2—Cl$	25	0.77
	50	(809)
$Ph—CHCl_2$	50	0.24
$Ph—CCl_3$	50	0.13

silver nitrate and allyl chloride, (b) a reaction of allyl chloride with silver nitrate in the presence of 0.2 *M* freshly prepared silver chloride, (c) a reaction of allyl chloride with silver nitrate in the presence of 0.2 *M* sensitized silver chloride. The data obtained are summarized in Table 4.

Table 4

Percentage of Silver Nitrate Reacted with Allyl Chloride after 180 Minutes in the Presence of an Excess of Silver Chloride in Absolute Alcohol

No.	Reactivities, %		
	(a)	(b)	(c)
1	9.08	11.06	13.3
2	9.21	11.07	15.4

Discussion

According to the currently prevailing theory there are two commonly occurring mechanisms for the nucleophilic substitution reactions: one is the bimolecular, kinetically second order substitution (SN 2) (Push type), or "Walden Inversion"[3] and the other is the ionization mechanism (SN 1) (Pull type).[4, 5, 2c] In the SN2 type mechanism, the driving force is chiefly a "Push" or nucleophilic backside attack by the atom or group having an unshared electron pair which is strongly dominant in the bond formation. On the other hand, in the SN 1 type or ionization mechanisms, the main part of the driving force is a "Pull" or front side attack by the solvent or some electrophilic reagent.[6] This weakens the old bond, allowing it to ionize in the rate determining step. This reaction is kinetically of the first order when it is with solvent which exists in large excess. The reaction of alkyl halide with silver nitrate is also the reaction of this type, though it is kinetically second order.

From the standpoint of the tetrahedral constitution of carbon atom, a steric hindrance is caused by the other three groups in the back side of the substituted group, therefore except in more complicated cases,[7] the hindrance must be considered in the SN 2 reaction, but not in the ionization or SN 1 reaction, when the reagent approaches to the reaction center.

There have been many reports concerning the extremely high reactivities of these compounds such as chloroacetone and benzyl chloride in the SN 2 type reaction,[8] and it might be considered from the authors' experiments that the high reactivities of chloroacetone, ω-chloroacetophenone and ethyl chloroacetate in SN 2 type reaction depend upon a low electron density in the α-carbon atom originated by the strong electron attractive effect of carbonyl group, thus making the approach of nucleophilic reagent easier. This interpretation appears to support the electrostatic hypothesis by Hinshelwood, Laidler and Timm.[9] The lower reactivties of these compounds in SN 1 type reaction (Pull-type) are also ascribed to the same reason — a lower electron density on the α-carbon atom, which attracts a pair of electron toward the carbon atom and makes the splitting of the chlorine anion more difficult. This argument is consistent with the hypothesis given by Hughes and Ingold.[10] The high reactivities of allyl chloride and benzyl chloride might be considered as such: as they have highly unsaturated group at α-carbon atoms, there arises the relatively high resonance energy in their transition states of both types of the reactions in common, thus making the ionization of chlorine easier.

The results obtained from the experiments of polychlorides can be well discussed as follows. The decrease of reactivities with the increase in the number of chlorine atoms in the reaction of polychlorides with potassium iodide might be ascribed to the steric hindrance, because the van der Waals' radius of chlorine is much larger than hydrogen. (Cl=1.8 Å, H=1.2 Å, cf., CH_3=2.0 Å).[11] The authors

(3) (a) Walden, *Ber.*, **28**, 1287 (1875).
(b) Hughes, Juliusburger, Massterman, Topley and Weiss, *J. Chem. Soc.*, **1935**, 1525.
(4) (a) Hughes, Ingold, *Nature*, **132**, 933 (1933).
(b) Hughes, *Trans. Farad. Soc.*, **37**, 602, 612 (1941).
(5) Recently G. Swain indicated that almost all the replacement reactions proceed through concerted mechanism and thereby the meanings of SN 1 or SN 2 have slightly altered out of their original meanings. Swain, *J. Am. Chem. Soc.*, **70**, 1119, 2989 (1948).
(6) Polanyi, *Endeavour*, **8**, 3 (1949).
(7) such as Brown's F-strain.
(8) Branch and Calvin, "Theory of Organic Chemisty", Prentice-Hall, Inc., 1941, pp. 428-440,
(9) Hinshelwood, Laidler and Timm, *J. Chem. Soc.*, **1938**, 848.
(10) Hughes, *J. Chem. Soc.*, **1946**, 968.
(11) Pauling, "The Nature of Chemical Bond", Cornell University Press, 1940, pp. 189.

consider that in the reactions with silver nitrate, the decreasing tendencies of reactivities of the *n*-butyl chloride series and the increasing trends of the benzyl chloride series with the increase in number of chlorine atoms are due to the following reasons. In the series of *n*-butyl chloride, the one chlorine atom, attaching to the simple alkyl group, cannot resonate largely in its transition state, but has the strong attractive inductive effect, thus making difficult the anionic dissociation of the other chlorine atom. On the other hand, in the series of benzyl chloride, chlorine atoms are attached to the carbon atom which can participate in the resonance system with phenyl group, thus making the electrons of the chlorine atoms resonate easily in its transition state. Therefore the one chlorine atom facilitate the ionization of the other chlorine atom, namely the reactivities are increased. Ingold, Hughes and their co-workers also support[12] the fact that in the reactions of alkyl series, the inductive effect is predominant in substitution or elimination, but in the aralphil series, the electromeric effect is prominent factor on their reaction rather than the inductive effect. This is quite in agreement with the results of the authors' experiments.

(12) (a) Hughes, Ingold and Taher, *J. Chem. Soc.*, **1940**, 949.
(b) Dhar, Hughes, Ingold, Mondour, Mau and Woolf, *J. Chem. Soc.*, **1948**, 2093.

Summary

(1) It was observed in the reaction of organic chloride with silver nitrate that the irregular catalytic action can be avoided by carrying experiments in a dark room.

(2) Silver nitrate was interacted with several organic chlorides which were highly reactive in SN2 type reaction and the kinetic data obtained were fully discussed.

(3) Some organic polychlorides were reacted with silver nitrate and with potassium iodide and rates obtained in these reactions were discussed.

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The "Critical Thickness" of Organic Thin Films[1]

With a Criticism to Long Range Force Hypothesis of Rothen

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Introduction

Several years ago, Rothen[2] postulated specific long range forces to explain the specific interaction of an antibody with the antigen layer through the inert screen film of the thickness extending over 150 Å. Since then, his proposal has aroused considerable interest in biologists, chemists and physists, and has become the focus of much controversy.[3],[4],[5],[6],[7] But anyone has not been able to formulate any such mechanism that could account for the specificity required to explain Rothen's experimental results. Rothen, himself, has suggested that this specific long range interaction might take place through resonating extended oscillators.

On the other hand, Singer[5] recently has shown the evidence that strongly suggests that holes in the screen films, permitting such macromolecules as antibody to come into contact and react with antigen, are primarily responsible for the effect observed by Rothen. We have also obtained experimental evidences that appear to suggest that the results of Rothen can be explained by a simpler mechanism that does not require the assumption of specific long range forces. This interpretation has been strongly supported by many facts that had already been obtained through the study of

(1) This paper was partly presented before the regular meeting of the Chemical Society of Japan held at Tokyo, Sept. 24, 1949, and the annual meeting of the Chemical Society of Japan held at Kyoto, Apr. 3, 1950.
(2) A. Rothen, *J. Biol. Chem.*, **168**, 75 (1947); *J. Am. Chem. Soc.*, **70**, 2732 (1948).
(3) F. Karush and B. M. Siegel, *Science*, **108**, 107 (1948).
(4) J. Iball, *Science*, **109**, 18 (1949).
(5) S. J. Singer, *J. Biol. Chem.*, **182**, 189 (1950).
(6) H. J. Trurnit, *Science*, **111**, 1 (1950).
(7) B. Carroll, *J. Am. Chem. Soc.*, **72**, 2763 (1950).

thin film. Then, we have found the "critical thickness" of thin film below which the film could not perfectly cover the substrate. There exist similar phenomena on metallic films. It is a well-known fact that metallic films given by evaporation and cathodic sputtering on non-conducting substrate display, below a certain thickness, different properties from those of the metals in bulk. These results have led us to an opinion that Rothen's results did not necessarily prove the existence of specific long range forces. The present paper describes the results of these experiments and some discussion thereupon.

Experimental Procedure and Results

Experiments have been made on three systems as follows: azo-ovalbumin—rabbit antisera against the haptenic group, azo-ovalbumin—ovalbumin, and cholestanol—digitonin.

1. Azo-ovalbumin—Antisera System.—In order to investigate whether specific long range action is demonstrated in artificial antigen—antisera system as well as natural antigen—antisera system used in Rothen's experiments, we have performed an experiment with azo-ovalbumin (ovalbumin coupled with diazotized *p*-amino-phenylarsonic acid) and antibody specifically directed against this haptenic group. After our studies were completed, we found that Singer carried out similar experiments on the same system. His works, however, differ from ours in respect to the condition of the film of antigen; his experiments deal with adsorbed film, while ours with unfolded film.

The techniques used in this experiment will be described elsewhere.(8) Azo-ovalbumin was prepared by coupling ovalbumin with diazotized *p*-amino-phenylarsonic acid in the usual manner. The number of the diazonium groups introduced in one ovalbumin molecule (assuming the molecular weight as 40,000) was found to be 47 analytically. Rabbit antisera was produced against horse globulin coupled with diazotized *p*-amino-phenylarsonic acid.

In order to prepare the antigen film, azo-ovalbumin was spread on distilled water and then, compressing the monolayer at surface pressure of 15 dynes per centimeter, one double layer of azo-ovalbumin was transferred onto the metal slide covered with an optical gauge of multilayers of barium stearate. Under these conditions, the thickness of the transferred antigen layer (one double layer) was found to be 26~30 Å. Subsequently, films of barium stearate, as screen, were deposited on the antigen films by means of the Blodgett—Langmuir technique. These slides were immersed into undiluted antiserum until the adsorption of the antibody was completed. After the slides were taken out of the solution, washed and dried, the increase of thickness was measured optically.

The experimental results are given in the curve A of Fig. 1. Each of the points represents an

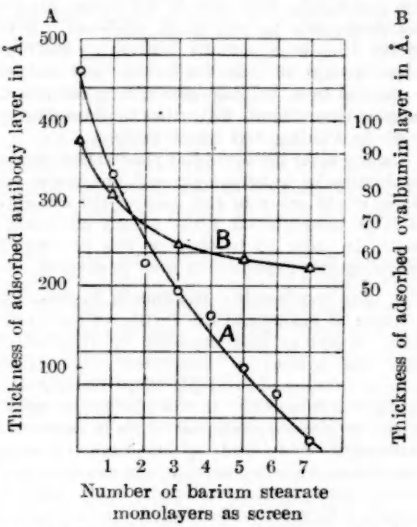

Fig. 1.—Screening action of barium stearate films on one double layer of azo-ovalbumin. Curve A, azo-ovalbumin—antiserum system; curve B, azo-ovalbumin—ovalbumin system.

average of about four independent determinations. Control experiments demonstrated that none of the antibody in the antiserum used in these experiments was adsorbed on the film of original ovalbumin when it was treated in the same manner, and that no measurable amounts of normal serum proteins were adsorbed on the stearate-coated or non-coated films of azo-ovalbumin. These results demonstrate that the antibody specifically directed against the haptenic group was adsorbed on the stearate-covered antigen through the screen in the range of thickness indicated.

Pauling, Pressman and Campbell,(9) on the other hand, based on the investigations of the hapten-conjugated antigen and the antibody, proposed a mechanism for the antigen-antibody reaction that, over a considerable portion of both molecules having complementary configuration, the short range forces, as van der Waals', electrostatic, hydrogen bond, and other similar forces could cooperate cumulatively to form a sufficiently strong bond.

In the case of azo-ovalbumin and antisera

(8) T. Tachibana, K. Fukuda, T. Ogata, K. Suzuki and S. Yamaoka, unpublished.

(9) L. Pauling, D. Pressman and D. H. Campbell, *Physiol. Rev.*, **23**, 203 (1943).

directed against the diazonium groups, antibody activity is directed specifically against them. If Rothen's interpretation is applied to our experiments, long range forces should operate between antibody and haptenic group of which chemical structure is well known. However, long range forces hypothesis was advanced on the basis of the assumption that holes in the screen films are not responsible for the effect observed. If thin screen films were actually preventing the diazonium groups of azo-ovalbumin and antibody molecules from coming into direct contact, this facts is inconsistent with the consideration put forth by Pauling and his co-workers.

On the other hand, similar phenomena observed by Rothen in immunologic and enzymatic reactions, might occur in the case of the adsorption of large molecule on films of any adsorbent as well. In order to investigate this problem, the following two experiments were performed.

2. Azo-ovalbumin—Ovalbumin System.—Adsorption of ovalbumin on the film of azo-ovalbumin. It was at first reported by Haurowitz[10] that the mixing of azoprotein and ovalbumin in solution of some *p*H range brought about precipitation reaction. In this case, the interaction would be of electrostatic nature as pointed out by Haurowitz. We found, by monolayer technique, that the ovalbumin molecule was adsorbed on the spread film of azo-ovalbumin when the slide covered with azo-ovalbumin film was brought into contact with the solution of ovalbumin. Then, experiments were extended to detect whether both molecules might not also exert their action throughout a screen film of barium stearate.

As described previously, ovalbumin coupled with diazotized *p*-amino-phenyl arsonic acid was spread on the distilled water and transferred, as one double layer, onto the metal slide covered with an optical gauge of multilayers of barium stearate. The thickness of one double layer was found about 28 Å. The number of the diazonium groups per molecule of the sample was found 58 analytically. Then azo-ovalbumin film was coated with the screen films of barium stearate in the same manner as in the previous experiments. Hereafter the slides to be tested (with or without screen) were immersed into the solution of *p*H 4 containing one percent of ovalbumin for 45 minutes at room temperature of about 10°C. The thickness increment was measured optically. The results (the thickness increment caused by the adsorption of ovalbumin) are given in curve B of Fig. 1. Ovalbumin molecules were adsorbed on azo-ovalbumin film, despite of the screen films of barium stearate over 100 Å. thick in a manner similar to that found for the antigen-antibody system. Control experiments demonstrated that ovalbumin layer of about 20 Å. thick was adsorbed directly on the stearate films alone, when they were treated in the same manner.

Rothen has performed, on the other hand, similar experiments with protamin and insulin to demonstrate that barium stearate and Formvar were effective screens for this system. A double layer of barium stearate covering the film of protamin clupein sulfate (10 Å. thick) cut down the adsorption of insulin completely, whereas 220 Å. of insulin could be adsorbed directly on the protamin. This fact was ascribed to the non-existence of holes in screens through which even smaller molecule, such as insulin, than antibody globulin molecule could permit to pass. However, as stated by Singer, the barium stearate screens may not be inert barrier in these experiments, but may rather react with the protamin film.

Such complications are excluded in our experiment with azo-ovalbumin-ovalbumin reaction. Therefore, the present results may show that apparently long range forces also might exert their effect in the reaction system mentioned above. The adsorption of ovalbumin on azo-ovalbumin film is commonly thought to be brought about due to the electrostatic forces between the oppositely charged molecules, since azo-ovalbumin molecule is charged negatively while ovalbumin molecule is positive at *p*H 4. Consequently, if long range force operates in this case, it may be of electrostatic nature. However, two possibilities may also be considered: 1) that there may be holes to permit the diffusion of ovalbumin molecules in the screens: 2) the electrostatic interaction between azo-ovalbumin film and ovalbumin molecule may take place through induced polarization through the screen. Which possibility is true, would be difficult to decide only from this experiment. At any events, it is important that there could be found a phenomenon that appeared to be caused by long range force, in non specific reaction also.

3. Cholestanol-Digitonin System.—The deposition of digitonin on cholestanol films was studied by Langumir, Schaefer and Sobotka.[11]

We have performed experiments to see whether the adsoption of digitonin does not take place through the screen of barium stearate. The techniques used are essentially the same as that described in their paper, except for the covering of cholestanol films with the screen of the built-up films of barium stearate.

The results are summarized in Table 1. It is noticeable that, regardless of the thickness of screens, the thickness increments after treatment with digitonin were found to be about 15 Å. Control experiment demonstrated that the optical gauge of stearate multilayers alone decreased 6 Å. in thickness after being treated with digitonin solution. The amount of digitonin adsorbed on cholestanol films was independent of the number of the monolayers of cholestanol on the slide. Although the amount of digitonin adsorbed on cholestanol film was independent of the thickness of screen films, the surfaces after adsorption of digitonin were, depending upon the thickness of

(10) F. Haurowitz, *Kolloid-Z.*, **74**, 208 (1936).

(11) I. Langmuir, V. J. Schaefer and H. Sobotka, *J. Am. Chem. Soc.*, **59**, 1751 (1937).

screen film, markedly different in their adhesion toward water. This is given in column marked "hydro-affinity" in Table 1. When screen films

Table 1

Screening Action of Barium Stearate Film against the Adsorption of Digitonin on Cholestanol Film

Cholestanol film		Screen of barium stearate		After treatment with digitonin		
Mode of deposition**	Thickness observed, Å.	Number of layers	Thickness observed, Å.	Thickness increment, Å.	Hydro-affinity of the surface	θ
AB	42	0	0	11	++	
$(AB)_2$	72	0	0	12.5	++	
$(AB)_5$	187	0	0	7	++	64°
AB	34	1	20.5	18.5	++	
AB	32	2	48.5	14	++	76°
AB	37	5	116	15	++	79°
AB	36	8	195	10	+	
AB	41	10	244	7	+	92°
				14.5*	+	

The time of adsorption was 10 minuutes in each experiment, but the value marked * was obtained by adsorption of one hour. Symbol ++ indicates to be more hydrophilic than symbol +. θ denotes the contact angle towards water. ** Symbols AB, $(AB)_2$ and $(AB)_5$ stand for one, two and five double layers, respectively.

of stearate are less than 5 monolayers, the slide has relatively high hydro-affinity. However, when they are thicker, the slide become less hydrophilic. Cholestanol films and barium stearate films themselves are both originally hydrophobic. Therefore, the effect observed might probably suggest that digitonin molecule, penetrating the screen film of stearate, came into contact directly with the underlying cholestanol film.

If this is the case, there may probably be holes to permit molecule as large as digitonin to diffuse in screen of stearate film.

Discussion

From the present studies, it was found that some kind of chemical reactions involving large molecule, such as the adsorption of ovalbumin on azo-ovalbumin film and the adsorption of digitonin on cholestanol film, as well as the adsorption of antibody on antigen film could occur although the adsorbent films were separated by the screen films of barium stearate. Consequently the phenomena that long range forces appear to operate are not always specific in biochemical reactions alone. Therefore, it seems to be unreasonable for us to require specific long range forces in immunologic and enzymatic reactions alone. It may be rather plausible to admit the possibility that holes in screen films are responsible for the effect observed, although Rothen attempted to show that the possibility did not exist or in any events was not important. At least, our experiment with the cholestanol-digitonin system might prove that there are holes to permit digitonin molecules to diffuse in screen film of barium stearate, since this system probably reacts by a short range mechanism.

Furthermore, we might show some evidences that the physical state of screen film is of fundamental importance for the explanation of the effect observed. Let us consider the barium stearate alone as screen film for convenience' sake.

If we examine the screening action of barium stearate films from the results of Rothen, Singer and the present authors, we see that there is an almost constant "critical thickness" of barium stearate films to inhibit the combination of antibody on antigen film.

This critical thickness is found around 150 Å. in most systems investigated, as summarized in Table 2. Particularly it would be difficult to explain from the long range forces hypothesis that the same value of critical thickness was obtained independently of whatever the antigens used may be natural or artificial, or whatever the amount of antibody adsorbed directly on antigen film may be (See Table 2).

The critical thickness of stearate film was also observed in other phenomena. The clean glass surface is hydrophilic and gives a zero

Table 2

The Critical Thickness of Barium Stearate Film to Inhibit the Specific Adsorption of Antibody on Antigen Layers

Varieties of the system	I One double layers of ovalbumin and anti-ovalbumin system	II One double layers of bovine albumin and anti-bovine albumin system	III Adsorbed layer of Pneumococcus polysaccharide III and homologous antibody system	IV Adsorbed human albumin and homologous antibody system	V One double layers of azo-ovalbumin and homologous antibody system
Thickness of antibody layer adsorbed directly on antigen film, Å.	26	65	270 125	80	465
Critical thickness of barium stearate film, Å.	70~100	150	150~190	150~160	150~170

Critical thickness was observed directly or calculated from the number of layers multiplied by the thickness per monolayer, 24.4 Å. I, II, III, were taken from the results of Rothen; IV from Singer; V from the present authors.

contact angle with water. However, after the stearic acid monolayers have been deposited on glass, the surfaces becomes hydrophobic and the contact angles increase with the number of the stearate monolayers until they attain a critical value, about 115°, where the thickness of stearate films is 70～120Å. (3～5 monolayers) as shown in Table 3 (column 3).

Table 3

Screening Action of Stearic Acid Multilayers on Solid Surface

1 Number of layers	2 Thickness, Å.	3 Contact angle towards water	4 Surface potential, mV.	5 Static friction coefficient
0	0	0°		1.0
1	24.4	66°11′ 101°46′	191	0.12
3	73	115°23′	355	0.09
5	122	115°56′	467	0.06
7	171	112°10′	457	0.06
9	220	117°36′		0.06

column 2 ; calculated from the thickness per monolayer, 24.4 Å.: column 3 ; S. Mitsui and T. Sasaki, private communication (1948): column 4 ; T. Isemura, Private communication (1950): column 5 ; T. Isemura, this Bulletin, **15**, 467 (1940).

The surface potential of stearate monolayers on metal slides shows also a similar behavior. In this case, the critical thickness of stearate monolayers is 120～170 Å. (5～7 monolayers) as indicated in column 4 of Table 3. It might also be significant to quote the results of Isemura who studied on the effect of monolayers on the static friction of glass surface. We see from his results that the static friction decreases with the increase of the number of stearate monolayers, until it becomes nearly constant in the region of the thickness exceeding five monolayers, *i.e.* about 120 Å., as shown in column 5 of Table 3. These results appear to be as if the character of underlying substance was transmitted across the screen film of stearate. Furthermore, as far as stearate films are used as screen, the critical thickness to interrupt the effect of underlying substance is always about 120 Å., irrespective of independent phenomena observed. This value of the critical thickness is approximately the same as that found in immunologic and enzymatic reaction. This coincidence is regarded as more than accidental. This seems to indicate that multilayers of stearate, when they are less than 150 Å. thick, consist of fragile structure. Namely such a thin film may be such as the network of structure loose enough to permit the diffusion or penetration of a large molecule. The detailed mechanism may be complicated. The present suggestion might be extended to apply to screen films of Formvar and other polymers as well.

Moreover, Rothen showed that in the bovine serum albumin—antiserum system, the amount of antibody adsorbed increased linearly with the number of monolayers of antigen up to eight layers where the thickness of adsorbed layer of antibody is 149 Å. We also obtained a similar relation from the experiments with azo-ovalbumin—rabbit antiserum. These results are represented in Fig. 2, the details of which will be described elsewhere.

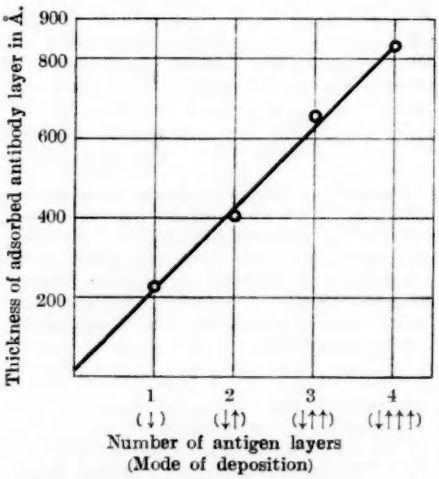

Fig. 2.—Relation between the number of azo-ovalbumin and thickness of antibody layer adsorbed on it.

It is noteworthy that a layer of 800 Å. of antibody, which is larger than the major axis of antibody molecule, was adsorbed directly on the four monolayers of antigen (ABBB). At first sight, this result might appear to support long range force hypothesis. However it may be unfavorable to Rothen's hypothesis that the thickness of antibody layer increases linearly with the number of underlying monolayers of antigen, *i.e.* the number of haptenic groups of antigen per unit area. The total haptenic groups of antigen layers should be available to the adsorption of antibody molecules. Let us notice that the thickness of antigen layer, in this experiment, is lower than the "critical thickness."

In this case, the structure of antigen layer may be fragile. Especially, by bringing into contact with antiserum, the structure of protein

layers may become more loose by swelling. Therefore, the antigen layer might conceivably disrupt, exposing all the haptenic groups of antigen molecules in original monolayers to antiserum. Thus, the underlying antigen layer, also, may become available to the reaction by direct contact with antibody molecules. After drying, the layers may become such structure as that in which antigens and antibodies are mixed together or alternated more regularly. Such conditions are probable in consideration of more strong affinity between antigen and antibody than between each antigen monolayers.

Rothen, also, reported that, on optical gauges of octadecylamine, a layer of 700 Å. of antibody was adsorbed on 5 Å. of pneumococcus type III polysaccharide. He explained this facts by long range forces. But, in this case also, as polysaccharide is a chain polymer, it may extend into bulk of antiserum, like seaweeds on the bed of sea, exposing all determinant groups to antibody. Therefore, adsorbed layer of 700 Å. is not a uniform layer of antibody, but instead may be quite complicatedly composed of antigen and antibody. Thus, the large thickness of $700 \sim 800$ Å. of adsorbed antibody layer observed by Rothen and us may be explained without long range forces hypothesis.

In conclusion, in view of the considerations and the evidences presented above, we seem to be facing the problem of a "critical thickness" or structure of thin organic films rather than the long range forces postulated by Rothen.

Summary

By studying the reactions of protein with the aid of monolayer technique, Rothen found that antigen and antibody, and also enzyme and substrate molecules, can react in despite of being apparently separated by some inert screen.

He assumed from these results, that the specific long range forces operate in immunologic and enzymatic reactions. We have found that similar phenomena occurred in the following systems: monolayer of hapten-conjugated protein as antigen and antibody directed specifically against the hapten, azo-ovalbumin and ovalbumin, and even cholestanol and digitonin. Therefore, it leaves some room for consideration to assume specific long range forces in immunologic and enzymatic reaction alone.

Besides, we suggested that there was required an almost constant thickness (about 150 Å.) of barium stearate to inhibit completely the combination of antibody with antigen in transferred film, independent of the variety of the systems.

We have also noticed, from the data of the contact angle towards water, those of surface potential and of static friction coefficient of stearic acid multilayers on glass or metal surface, that the multilayers of stearic acid must have a thickness over about 150 Å. (same as the result of antigen-antibody reaction) to interrupt the effect of underlying substance, regardless of the phenomena concerned.

These facts appear to suggest the fragile nature of screen film which is thinner than the certain thickness which we call the "critical thickness." Such a thin film may conceivably be such as the net-work structure loose enough to permit the diffusion and the penetration of large molecules. Such a physical state of screen film may primarily be responsible for the results of the experiments of Rothen, Singer and the present authors.

The authors are grateful to Professor Jitsusaburo Sameshima and Professor Tomio Ogata for their continual help and advice. Some of the samples were prepared by Dr. Kan Suzuki and Dr. Seizaburo Yamaoka; the authors are indebted to them for their assistance. The expense of this work has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the authors' thanks are due.

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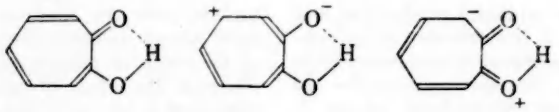
Dipole Moments of Tropolone and Related Compounds[1]

By Yukio KURITA, Tetsuo NOZOE and Masaji KUBO

(Received September 15, 1950)

Introduction

One of us[2] carried out extensive studies on the chemical properties of hinokitiol (4-isopropylcycloheptatriene-2, 4, 6-ol-2-one-1) and assumed its structure to be the resonance hybrid among various electronic structures of



A B C

type A, B and C. He[3] also succeeded in synthesizing this compound and its mother substance, tropolone (cycloheptatriene-2, 4, 6-ol-2-one-1). We measured the dipole moments of some of these compounds in benzene solution. The object of the present work is twofold. The first is to obtain some conclusion concerning the positions of substituents in various substituted tropolone and hinokitiols. The second is to investigate the structure of cycloheptatrienolone ring. This is of interest because the ring has odd number of carbon atoms. Wheland and Mann[4] have measured the dipole moment of azulene, but in general the data on cycloheptatriene ring compounds are very scanty. It will be very desirable to determine whether the cycloheptatrienolone ring is planar like benzene ring or non-planar like cyclooctatetraene ring.

Experimental Method and Materials

Die'lectric constants were measured by heterodyne beat method at the wavelength of 300 m. The sum of P_E and P_A was taken to be equal to the molecular refraction for D-line calculated additively from the atomic refractions of constituent atoms and bonds. This did not cause any serious error because orientation polarizations are very great. The materials used were prepared by one of us[2][3] and his collaborators. They are :— tropolone, m. p. 51°, tribromotropolone, 126°, hinokitiol, 52°, α-monobromohinokitiol, 56°, α-dibromohinokitiol, 134°, β-dibromohinokitiol, 96°, α-mononitrohinokitiol, 56°, dinitrohinokitiol, 155°.

Experimental Results

The results obtained are shown in Table 1, where w and P denote the weight fraction and molecular polarization respectively. Other notations used have their usual significances.

Table 1

Dipole Moments of Tropolone and Related Compounds

w_2(%)	ε_{12}	d_{12}	P_2(cc.)
Tropolone, 25° and 35°			
0	2.273	0.8733	(317.5)
0.621	2.346	0.8749	295.5
1.332	2.421	0.8764	277.2
1.951	2.487	0.8784	268.7
$P_{2\infty}$ = 317.5 cc., R_D = 32.5 cc., μ = 3.71 D			
0	2.253	0.8627	(298.0)
0.621	2.321	0.8645	282.1
1.332	2.395	0.8659	272.3
1.951	2.460	0.8682	265.0
$P_{2\infty}$ = 298.0 cc., R_D = 32.5 cc., μ = 3.64 D			
Tribromotropolone, 25°			
0	2.273	0.8733	(125.6)
0.604	2.280	0.8769	122.4
1.145	2.291	0.8800	147.5
1.830	2.305	0.8840	157.5
$P_{2\infty}$ = 125.5 cc., R_D = 55.7 cc., μ = 1.84 D			
Hinokitiol, 33°			
0	2.257	0.8651	(375)
2.047	2.467	0.8687	351
3.002	2.573	0.8706	350
3.686	2.628	0.8715	334
$P_{2\infty}$ = 375 cc., R_D = 46 cc., μ = 4.04 D			

(1) Presented at the Annual Meeting of the Chemical Society of Japan on 2 April 1950 and at the General Discussion on Structural Chemistry held by the society on 8 July 1950.

(2) T. Nozoe, *Yakugaku*, **3**, 174 (1949).

(3) T. Nozoe *et al.*, *Proc. Japan Acad.*, **26**, 38, 43, 47 (1950).

(4) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

w_2(%)	ε_{12}	d_{12}	P_2(cc.)
α-Monobromohinokitiol, 33°			
0	2.257	0.8651	(430)
2.047	2.420	0.8724	411
2.448	2.454	0.8738	404
3.055	2.505	0.8762	402

$P_\infty = 430$ cc., $R_D = 54$ cc., $\mu = 4.32$ D

α-Dibromohinokitiol, 33°

0	2.257	0.8651	(430)
1.208	2.329	0.8710	409
2.334	2.391	0.8756	393
3.941	2.486	0.8832	386

$P_\infty = 430$ cc., $R_D = 62$ cc., $\mu = 4.27$ D

β-Dibromohinokitiol, 20°

0	2.283	0.8790	(269)
0.4351	2.302	0.8809	317
0.6964	2.317	0.8821	342
0.9113	2.332	0.8832	368

$P_\infty = 269$ cc., $R_D = 62$ cc., $\mu = 3.14$ D

α-Mononitrohinokitiol, 25°

0	2.273	0.8733	(847.3)
0.558	2.387	0.8753	824.3
1.212	2.522	0.8769	807.5
1.526	2.582	0.8777	788.7

$P_\infty = 847$ cc., $R_D = 53$ cc., $\mu = 6.19$ D

Dinitrohinokitiol, 20°

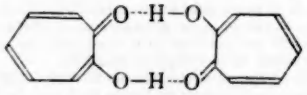
0	2.283	0.8790	(537)*
2.450	2.534	0.8874	506

$P_\infty = 537$ cc., $R_D = 59.5$ cc., $\mu = 4.63$ D

* Hedestrand's method of extrapolation (*Z. physik. Chem.*, B, **2**, 428(1929).) was used for this as well as for others giving values consistent with those extrapolated graphically.

Discussion

The dipole moments of these compounds are high. Hence the existence of dimers with a vanishing moment such as (I) cannot be conceivable. The normal dependence of molecular polarization upon concentration also denies such association. The bonds of high moments in the molecules of tropolone and hinokitiol are located in the part of -CO-C(OH)-. Assuming the bond moments of C=O, C-O and O-H to be equal to 2.5 D, 0.86 D and 1.53 D respectively, the valency angle ∠C-O-H to be 110° and that of ∠C-C-C at the C-atom of carbonyl group to be 130° as in benzophenone,[5] the resultant moment is calculated as 2.1 D, if the valency angle ∠C-C-O at the C-atom of C-OH is equal to the tetrahedral angle. The resultant moment is fairly insensitive to the assumed value of the ∠C-C-O angle. In fact, it is 2.0 D if the latter angle is equal to 115.7° which corresponds to the regular heptagon form of the ring and 1.85 D if the angle is assumed to be 120°. The difference between these and the observed values are too great to be attributable to the solvent effect or induction effect. We must take into account the hydrogen bond between the H-atom in OH and the O-atom in C=O and resonance among various electronic structures of the type B with a formal positive charge at one of the seven C-atoms in the ring. There will be fourteen such electronic structures if the two O-atoms can interchange their role. Each of these structures, to be sure, corresponds to an excited state with smaller number of double bonds. Hence its contribution to the normal state will be small. But the number of these dipolar-ionic structures are great and each of these structures has very high moment. These two factors will be sufficient to account for the observed moments. Furthermore the fact that tropolone and its derivatives show fairly strong acidic character and that they are readily attacked by electrophilic reagents giving substitution products suggests the possibility of resonance involving the electronic structures of type C. Their contribution, however, will be small. The rather small contribution of the electronic structures of type C is in agreement with our results concerning the direction of dipoles in the molecules as will soon be evident.



(I)

As a result of resonance among these structures, it is supposed that each bond in the ring has a certain amount of double bond character and the cycloheptatriene ring takes a plane form. The valency angle of carbon must deviate from its normal value and consequently internal energy will increase. We calculated the hybridization of $2s$, $2p_x$ and $2p_y$ orbitals giving three hybrid orbitals ψ_1, ψ_2, ψ_3 the latter two of which are equivalent and make an angle θ with each other. It was found that, as shown in Table 2, the bond strengths for θ equal to the angle of a regular heptagon 128°34′ are weakened about 0.6% in

(5) N. L. Leonard and L. E Sutton, *J. Am. Chem. Soc.*, **70**, 1564(1948).

Table 2

Bond Strengths of sp^2-Hybrid Orbitals

θ	ψ_1	ψ_2, ψ_3
109°28′	1.932	2.000
120°	1.991	1.991
128°34′	1.999	1.979

the two equivalent orbitals ψ_2, ψ_3 to be assigned to the bonds in the ring and strengthened about 0.4% in a non-equivalent orbital ψ_1 for the bond to a substituent as compared with the benzene ring. Though in total the bond strengths become weak, the small increase of energy of this magnitude will be overcompensated by high resonance energy[6] due to a great number of resonating structures stabilizing the molecules. It should be noted that if instead of bond strength, the dependence of bond energy, calculated by Penney[7] from resonance integrals, upon the angle θ is considered, the formation of heptagon ring becomes more favorable.

Finally the position of substituents in various derivatives must be determined. A difficulty arises because, though the magnitude of dipole moment of hinokitiol has been measured, the direction of dipole in the molecule cannot be obtained experimentally. The approximation is reasonably adequate that the moment of monobromohinokitiol is the vector sum of that of hinokitiol μ_0 and C-Br bond moment (μ(C-Br)=1.48 D). It is highly probable from the consideration on the course of formation[1] of α-monobromohinokitiol that Br-atom is in the position 7. Therefore, a plane heptagon form of the ring being assumed, the C-Br moment points along a line from the center of the ring to the C-atom at the position 7. The angle between this and μ_0 can be determined since their vector sum is known. There are two possibilities in the direction of μ_0, one to each side of C-Br bond moment. Considering various resonating structures of type B, μ_0 pointing in the direction nearly coincident with the line from the center of the ring to the middle point of two O-atoms with positive end at the ring[8] is taken to be correct. The other possibility with the dipole nearly pointing in the opposite direction must be rejected.[9]

The magnitude and the direction of the dipole moment of hinokitiol being known, the moment of tropolone can be calculated by subtracting vectorially the bond moment of isopropyl group, which is assumed to be equal to that of isopropylbenzene[10] (μ(C-i-C_3H_7)−μ(C-H)=0.65 D). The calculated moment is 3.8 D in agreement with the observed value 3.7 D. For bromo- and nitro-derivatives, the conceivable position of substitution are 3, 5 and 7 in analogy to benzene derivatives such as phenol or aniline.[11] The calculated moments of dibromohinokitiols are 3.7 D, 4.7 D and 2.9 D for 3,5-, 3,7- and 5,7-dibromohinokitiol respectively. Comparing these values with the observed ones, it is concluded that the position of substituents in α-dibromohinokitiol is 3,7 while in β-dibromohinokitiol it is 5,7.[12] Assuming the bond moment of nitro-group to be μ(C-NO_2)−μ(C-H)=3.0 D, the moment of mononitrohinokitiol is calculated to be 6.0 D, 1.3 D and 5.1 D for 3-, 5- and 7-nitrohinokitiol. Comparing these values with the observed one, the probable positions of a substituent group in α-mononitrohinokitiol is supposed to be 3 or 7. The calculated moments of dinitrohinokitiols are 4.1 D, 5.4 D and 2.6 D for 3,5-, 3,7- and 5,7-dinitrohinokitiol respectively. Comparing these values with the observed one, it is supposed that dinitrohinokitiol under investigation is 3,5- or 3,7-derivative. The reason for the indefinite conclusions are partly connected with the magnitude of C-NO_2 bond moment that must be assumed.[13] For tribromotropolone, all the three positions 3, 5 and 7 must be substituted by Br-atoms. The moment calculated from that of tropolone and three C-Br bond moments is 2.8 D, which is much higher than the observed value. If, however, the moments of C=O, C-OH are added vectorially together with three C-Br and two C-H moments in accordance with the electronic structure of the type A without

(6) We (Y. Kurita and M. Kubo, this Bulletin, **24**, 13 (1951)). have carried out molecular orbital treatment on tropolone and obtained high resonance energy.

(7) W. G. Penney, *Proc. Roy. Soc.*, A, **146**, 223 (1934).

(8) The molecular orbital treatment on tropolone also gives a moment in the direction along the line from the center of the ring to the middle point of the two O-atoms, with a positive end at the ring.

(9) It can be shown that the latter possibility gives resultant moments for dibromo-derivatives that never agree with experiments.

(10) J. W. Baker and L. G. Groves, *J. Chem. Soc.*, **1939**, 1144.

(11) By the molecular orbital treatment already mentioned, it is found that in the molecule of tropolone, π-electron distribution is concentrated at C-atoms 3, 5 and 7, which justifies that only these positions are liable to be attacked by electrophilic reagents.

(12) 3,5-Dibromo derivative can be excluded also from considerations in organic synthesis. Both α- and β-dibromohinokitiol can be obtained from α-monobromohinokitiol by bromination[2].

(13) Considering the neglection of possible formation of hydrogen bond between the H-atom in OH and the O-atom in the neighboring nitro-group and the consequent existence of tautomers and taking into account the investigations on the rearrangement product of this compound[3], we should like to reserve, for a while, definite conclusions concerning the positions of substituent groups. Final decision must be given after investigations are extended to cover wider scope of compounds of related structure.

considering resonance effect, the calculated value is 1.8 D in close agreement with experiment. Probably unshared electron pairs of Br-atoms in competition with that of O-atom decrease the resonance effect and consequently diminish the localization of positive charge on the ring, which is characteristic to tropolone. Furthermore, the electron withdrawal by three electronegative Br-atoms decreases the electron density in the ring, rendering the contribution of the electronic structure of type B more difficult or that of type C more important in conformity to the experimental observations that Br-substituted tropolone and hinokitiol are more strongly acidic than their mother substances.

Summary

The dipole moments of tropolone (cycloheptatriene-2,4,6-ol-2-one-1) and related compounds were measured in benzene solution. The values obtained are:— tropolone, 3.71 D (25°) and 3.64 D (35°); tribromotropolone (3,5,7-tribromo-), 1.84 D(25°); hinokitiol(4-isopropylcycloheptatriene-2,4,6-ol-2-one-1), 4.04 D (33°); α-monobromohinokitiol (7-bromo-), 4.32 D (33°); α-dibromohinokitiol (3,7-dibromo-), 4.27 D (33°); β-dibromohinokitiol (5,7-dibromo-), 3.14 D (20°); α-mononitrohinokitiol (3- or 7-nitro-), 6.19 D (25°); dinitrohinokitiol (3,5- or 3,7-dinitro-), 4.63 D (20°). The high dipole moments of tropolone and hinokitiol were explained adequately by taking into consideration the contribution of various resonance structures with a formal positive charge at the ring C-atoms. The resonance was supposed to give a certain amount of double bond character to each bond in the ring, causing plane cycloheptatrienolone ring. The position of substituents in the substituted tropolone and hinokitiols were determined and are given immediately after each name of these compounds in parentheses.

We wish to express our cordial thanks to Prof. S. Seto, Mr. Y. Kitahara and Mr. T. Mukai of Tohoku University for collaborating with us in the syntheses of these new compounds and to Prof. A. Kotera for lending us his experimental apparatus. Our thanks are also due to the Ministry of Education in aid of this research.

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Molecular Orbital Treatment of Tropolone[1]

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In the previous paper[2] we measured the dipole moment of tropolone (cycloheptatriene-2,4,6-ol-2-one-1) and its derivatives[3] and discussed the molecular structure of these compounds. We arrived at the conclusion that these molecules resonate among various electronic structures contributing to the normal states of these molecules and that each bond in the ring has a certain amount of double bond character causing plane cycloheptatrienolone ring. We found that the dipole moments of tropolone and hinokitiol (4-isopropylcycloheptatriene-2,4,6-ol-2-one-1) are nearly pointing along the line from the center of the ring to the middle point of two O-atoms with a positive end at the ring. The positions of substituents in the substituted tropolone and hinokitiols were determined, though for a few of them two alternatives were given to be decided finally by further investigations.

The theoretical investigations on the conjugated double bonds by the method of molecular orbitals have already been applied to the molecules of various compounds and have succeeded in the elucidation of the geometrical structures of these molecules, dipole moments, resonance energies, absorption spectra, chemical reactivities, etc. In the present paper we wish to report the results of application of the method of molecular orbitals to tropolone and show

(1) Presented at the General Discussion on Structural Chemistry held by the Chemical Society of Japan on 8 July 1950.

(2) Y. Kurita, T. Nozoe and M. Kubo, this Bulletin, **24**, 10 (1951).

(3) T. Nozoe *et al.*, *Proc. Japan Acad.*, **26**, No. 7, 38, 43, 47 (1950).

that the results obtained experimentally are reasonably correct from theoretical considerations. Finally we shall give the characteristic properties of cycloheptatriene ring.

In the LCAO-molecular orbital method, each electron is considered to be in the self-consistent field due to other electrons and atomic nuclei and the single electron wave function ψ_j is approximated by a linear combination of atomic orbitals φ_k, each belonging to one of the nuclei. We treat the problem as a π-electron system, excluding, for a while, σ-electrons involved in the formation of single bonds.

$$\psi_j = \sum_k a_{jk}\varphi_k$$

The electronic energy E_j of the molecular orbital ψ_j can be obtained as roots $E=E_j$ $(j=1, 2, .. l)$ of a secular equation,

$$D = H_{mk} - S_{mk}E = 0,$$

where l denotes the number of π-electron atomic orbitals and H_{mk} and S_{mk} are given by the following equations respectively.

$$H_{mk}=\int \varphi_m^* H \varphi_k d\tau, \quad S_{mk}=\int \varphi_m^* \varphi_k d\tau.$$

The coefficients a_{jk} can be calculated by solving a set of simultaneous equations,

$$\sum_{k=1}^{l} a_{jk}(H_{mk}-S_{mk}E_j)=0, \quad j, m=1, 2..l,$$

and normalizing the wave function ψ_j. The wave function for the ground state can be obtained if we allot all π-electrons successively to the molecular orbitals ψ_j of low energy E_j, with the restriction that only two electrons of opposite spin can be adopted by each orbital.

An electron in the molecular orbital ψ_j spends a fraction $|a_{jk}|^2$ of time in the atomic orbital φ_k. Consequently the mean number of π-electrons at k-atom is given by

$$q_k = \sum_j |a_{jk}|^2,$$

where the sum extends over all molecular orbitals ψ_j occupied by electrons in the ground state. The bond order p_{lm} was defined by Coulson[4] as

$$p_{lm} = \sum_j a_{jl}a_{jm}.$$

The sum of bond orders relating to l-atom, *i. e.*,

$$N_l = \sum_m p_{lm}$$

expresses the saturation degree of valency of l-atom. Coulson[5] defined the free valence index of l-atom by

$$F_l = N_{\max} - N_l$$

and gave to $N_{\max}$ (the maximum value of N_l) the value of 1.68 for carbon. The free valence index is a measure of reactivity of the atom towards a free radical. The constitutional formula with the inscription of values of q_k, p_{lm} and F_l is called a molecular diagram.[6]

In actual calculation for a molecule under investigation, we make the approximation that H_{mk} is zero except Coulomb integrals H_{kk} and exchange integrals between neighboring atoms, since exchange integrals will decrease rather rapidly as the distance between the atoms increases. In a similar manner, as for the matrix components of unity, the overlap integrals are assumed to be $S_{mk}=0$, while $S_{kk}=1$. We now introduce, for the convenience of calculation, two quantities δ_k and ρ_{mk} defined by[7]

$$H_{kk}=\alpha_k=\alpha+\delta_k\beta, \quad H_{mk}=\beta_{mk}=\rho_{mk}\beta,$$

where α is the Coulomb integral of an electron in a π-orbital of benzene molecule, and β is the exchange integral between neighboring C-atoms in the same molecule.

The calculation of successive approximation must be carried out until the final result is self-consistent.[8] First a set of proper values is chosen for δ_k and ρ_{mk}, *i.e.*, for α_k and β_{mk}. These enable us to calculate molecular orbitals, which in turn give q_k and p_{mk}. The total charge Q_k of each atom in the molecule and the interatomic distance r_{mk} between neighboring atoms can be obtained from q_k and p_{mk} respectively. Then α_k and β_{mk} are calculated from Q_k and r_{mk} respectively. The calculated values will not in general be identical with the original set. The calculations are repeated with the new set. This procedure is continued until the assumed set and the calculated set are almost identical. Four functional relations between q_k and Q_k, Q_k and α_k, r_{mk} and β_{mk}, p_{mk} and r_{mk} are required for the calculation. We used the following interrelations. (i) The total charge Q_k belonging to each atom is

(4) C. A. Coulson, *Proc. Roy. Soc.* (London), A, **169**, 423 (1939).

(5) C. A. Coulson, *Chem. Abstr.*, **43**, 6877 (1949).

(6) A. Pullman, B. Pullman and P. Rumpf, *Bull. soc. chim. France*, **1948**, 757. B. Pullman and G. Berthier, *ibid.*, **1948**, 788.

(7) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

(8) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

equal to the sum of the nuclear charge, the charge of electrons in an inner shell, π-electron density q_k and σ-electron density, which is given by $\sum(l)\ \mu_{kl}/r_{kl}$, where μ_{kl} and r_{kl} denote respectively the dipole moment of σ-bond and interatomic distance between k- and l-atom. The sum is over all σ-bonds attached to the k-atom. (ii) According to Sandorfy,[9] α_k is proportional to the electronegativity χ_k of an atom. Assuming $\alpha/\beta=4.1$, the values of δ_k are calculated as shown in Table 1. For an

Table 1

Electronegativity χ_k and δ_k

Atom	χ_k	δ_k
C	2.50	0.00
N	3.15	1.07
O	3.60	1.80
F	4.15	2.70

atom with a charge Q_k correction term must be added. According to Pauling[10] a unit positive formal charge increases the electronegativity of an atom by an amount approximately equal to two-thirds of the difference between the electronegativities of that atom and the next atom to the right in the periodic table, and a negative formal charge similarly decreases the electronegativity value. Hence for an a-atom with a charge Q_k, the electronegativity χ_k is given by

$$\chi_k = \chi_a + \frac{2}{3}(\chi_b - \chi_a)Q_k,$$

where χ_b denotes the electronegativity of a b-atom, the right neighbor of the a-atom. From the proportionality of electronegativity and Coulomb integral, $\alpha_k=(\chi_k/\chi_C)\alpha_C=\alpha_C+(\chi_k/\chi_C-1)d_C$, and by definition, $\alpha_k=\alpha_C+\delta_k\beta$. Hence

$$\delta_k=\left(\frac{\chi_k}{\chi_C}-1\right)\frac{\alpha_C}{\beta}.$$

Inserting in this equation the value of χ_k obtained above,

$$\delta_k=\left[\left(\frac{\chi_a}{\chi_C}-1\right)+\frac{2}{3}\left\{\left(\frac{\chi_b}{\chi_C}-1\right)-\left(\frac{\chi_a}{\chi_C}-1\right)\right\}Q_k\right]\frac{\alpha_C}{\beta}=\delta_a+\frac{2}{3}(\delta_b-\delta_a)Q_k.$$

Hence for carbon

$$\delta_k=\frac{2}{3}\delta_N Q_k=0.71Q_k,^{(11)}$$

and similarly for oxygen

$$\delta_k=1.80+\frac{2}{3}(\delta_F-\delta_O)\,Q_k=1.80+0.60Q_k,$$

$$\delta_k=1.80+\frac{2}{3}(\delta_O-\delta_N)\,Q_k=1.80+0.49Q_k,$$

for $Q_k>0$ and $Q_k<0$ respectively. Considering the polarization of σ-bonds, the value of δ for a C-atom neighboring to a hetero-atom was assumed to be equal to one-tenth of δ of the latter atom. (iii) The exchange integral β_{mk} was assumed by Sandorfy[9] to be inversely proportional to the fourth power of interatomic distance r_{mk}. (iv) The relation between the bond order p_{mk} and interatomic distance r_{mk} is given by Coulson's curve[4] for C-C bonds. We calculated the bond order of C-O bonds for various compounds as shown in Table 2. Approximately linear relation is obtained between the bond order and the interatomic distance.

Table 2

Interatomic Distance and Bond Order of C-O Bonds

	Interatomic distance	Bond order
Single bond	1.43	0
Resorcine	1.36	0.28
$CaCO_3$	1.31	0.58
$NaHCO_3$	1.27	0.68
Double bond	1.22	0.94
Double bond*	1.185	1

* Ideal double bond with no ionic character[12]

Molecular Diagram of Tropolone.—The C-atoms of tropolone are numbered in the same way as the nomenclature "cycloheptatriene-2, 4, 6-ol-2-one-1." Let us call the two O-atoms attached to the position 1 and 2 respectively by the number 8 and 9. Molecular orbitals are constructed from π-orbitals belonging to these nine atoms. The number of electrons to be put in these orbitals is ten, *i. e.*, eight electrons for double bonds plus two electrons for a lone pair at one of the O-atoms. Though the two O-atoms are not exactly equivalent, they are supposed to be nearly so, owing to the hydrogen bond formation and resonance. Therefore we assign to each of them a charge of $+1.5\,e$ for the sum of the charge of a nucleus and electrons in an inner shell and a charge $-0.12\,e$ due to the

(9) C. Sandorfy, *Bull. soc. chim. France*, **1949**, 615.
(10) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York (1948), p. 66.
(11) Wheland and Mann[6], in calculating the dipole moment of fulvene, assumed the coefficient to be equal to 1 instead of 0.71.
(12) R. Cantarel, *Bull. soc. chim. France*, **1949**, M 327.

polarization of O-H σ-bond. Consequently the molecule is assumed to be symmetrical across a plane through C-atom 5 and the middle point of C-atoms 1 and 2, and perpendicular to the ring. As a zeroth approximation we put $\rho_{mk}=1$, $\delta_8=\delta_9=2$ and $\delta_k=0$ for C-atoms. Calculation gives for the dipole moment due to π-electrons the value of $\mu_\pi=8.7$ D. The first and the second approximations give 6.7 D and 4.4 D respectively. The molecular orbitals for the last calculation in the order of increasing energy are found to be

$$\psi_S(-2.773)=0.442(\varphi_9+\varphi_8)+0.489(\varphi_2+\varphi_1)+0.222(\varphi_3+\varphi_7)+0.114(\varphi_4+\varphi_6)+0.084\varphi_5,$$

$$\psi_A(-2.131)=0.574(\varphi_9-\varphi_8)+0.338(\varphi_2-\varphi_1)+0.213(\varphi_3-\varphi_7)+0.104(\varphi_4-\varphi_6),$$

$$\psi_S(-1.765)=0.224(\varphi_9+\varphi_8)+0.066(\varphi_2+\varphi_1)-0.241(\varphi_3+\varphi_7)-0.479(\varphi_4+\varphi_6)-0.562\varphi_5,$$

$$\psi_A(-1.137)=-0.289(\varphi_9-\varphi_8)+0.061(\varphi_2-\varphi_1)+0.465(\varphi_3-\varphi_7)+0.444(\varphi_4-\varphi_6),$$

$$\psi_S(-0.572)=0.437(\varphi_9+\varphi_8)-0.292(\varphi_2+\varphi_1)-0.359(\varphi_3+\varphi_7)+0.105(\varphi_4+\varphi_6)+0.409\varphi_5,$$

where the suffixes S and A donote the symmetry properties of the wave functions, and the number in the parentheses give $y_j=(\alpha-E_j)/\beta$,[13] instead of E_j. The results for the ground state,

$$\psi_S^2(-2.773)\psi_A^2(-2.131)\psi_S^2(-1.765)\times\psi_A^2(-1.137)\psi_S^2(-0.572)$$

are given in the molecular diagram depicted in Fig. 1.

The direction and the magnitude of the dipole moment of tropolone have been determined in the previous paper[2] and is shown in Fig. 2. The π-moment can be obtained by

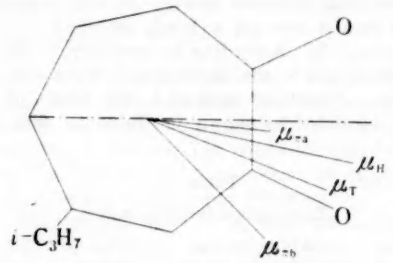
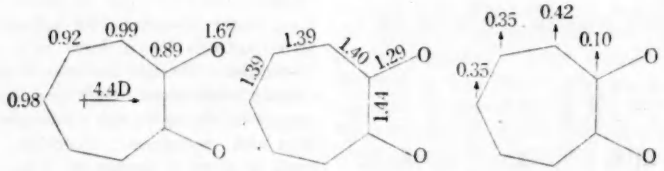


Fig. 2.—Dipole moment of tropolone: $\mu_H=4.04$ D, hinokitiol; $\mu_T=3.7$ D, tropolone; $\mu_{\pi a}=2.4$ D, $\mu_{\pi b}=3.3$ D, π-moment of tropolone.

subtracting two C-O bond moments (μ(C-O)=0.86 D), one O-H bond moment (μ(O-H)=1.53 D), and five C-H bond moments (μ(C-H)=0.40 D). The results is $\mu_{\pi a}=2.4$ D if hinokitiol is 4-isopropylcycloheptatriene-2, 4, 6-ol-2-one-1, or $\mu_{\pi b}=3.3$ D if the compound is isopropylcycloheptatrienol-1-one-2. The direction of the dipole moment $\mu_{\pi a}$ thus obtained is nealy coincident with the result of molecular orbital treatment. As regards its magnitude, the calculated value is still greater than the observed one. Further approximation will be necessary to reach perfect agreement.

All C-atoms in the ring have a mean number of π-electrons less than unity, indicating that π-electrons are displaced from the ring. The π-electron distribution suggests that electrophilic atoms and radicals will attack the C-atoms 7 (ortho'[14]), 3 (ortho) and 5 (para), the former two being more liable to be attacked than the latter. This justifies our assumption made in the previous paper that only C-atoms 7, 3 and 5 are to be considered for the position



π-Electron distribution | Interatomic distances | Free valence indices

Fig. 1.—The molecular diagram of tropolone.

(13) Since β is negative, the lower the energy E_j is, the smaller the value of y_j.

(14) T. Nozoe, *Yakugaku*, **3**, 174 (1949).

of substituents such as a Br-atom or a nitro-group and that α-monobromohinokitiol is 7-bromohinokitiol.[15] The free valence indices indicate that reagents of free radical type will react at C-atoms 7 and 3.

The total energy is found to be $10\alpha + 16.756\beta$, while that of the electronic state represented by an ordinary constitutional formula without taking into account the resonance effect is $10\alpha + 13.664\beta$. Hence resonance energy is 3.09β, as compared with 2β for benzene. This accounts for the aromatic character of tropolone-type molecules.

As has already been mentioned, it is almost certain from the theoretical considerations as well as from experimental results that in tropolone and its derivatives electrons are displaced away from the ring. It seems very probable that the same effect occurs in the case of other compounds with cycloheptatriene ring. In fact, Berthier and Pullman[16] have carried out molecular orbital treatment on methylene-cycloheptatriene and calculated its dipole moment to be equal to 2.35 D with the positive end at the ring. It seems appropriate to mention in this connection that they studied also fulvene with a cyclopentadiene ring, and found a moment of 3 D with the negative end at the ring. In fact, these tendencies reveal themselves in condensed rings as well as in the case of hyperconjugation. The characteristic electron distribution seems to be the cause of the peculiar properties of tropolone-type compounds in general.

(15) The position 3 (ortho) will be more difficult to be attacked than 7 (ortho') owing to steric effect.

(16) G. Berthier and B. Pullman, *Bull. soc. chim. France*, **1949**, D 457.

Summary

The molecular orbital treatment was carried out on tropolone. The π-electron distribution, interatomic distances, free valence indices and dipole moment were derived. It was found that the dipole moment is very high (second approximation value of π-electron moment = 4.4 D) owing to resonance and lies along a line from the center of the ring to the middle point between two O-atoms with its positive end at the ring and that the resonance energy amounts to about 1.5 times that of benzene in general agreement with experimental results. It was shown that the substitution by electrophilic atoms and groups are most liable to occur at C-atoms 7, 3 and 5.

We wish to express our thanks to Prof. T. Nozoe of Tohoku University for his interest on this subject and many valuable discussions from organic chemical point of view. Our thanks are also due to the Ministry of Education in aid of this research.

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Studies on Amino-hexoses. I. A New Method for Preparing Crystalline D-Arabinose

By Yoshio MATSUSHIMA

(Received September 18, 1950)

The preparation of D-arabinose has been dependent on the methods of Ruff,[1] of Wohl-Zemplen[2] or of Weermann[3], all of which being consisted of degrading D-glucose.

The author took up D-glucosamine as a starting material which is much accessible in this country. The author's aim was that D-glucosamine, a sort of α-amino-aldehyde, would undergo an oxidation analogous to the oxidation of α-amino-acids as exhibited by Dakin[4] and Langheld[5] who obtained aldehydes with one carbon atom less than the starting amino-acids. In fact, Herbst[6] has oxidized glucosamine with chloramine-T (*p*-toluenesodium sulfonchloramide) and has

(1) O. Ruff, *Ber.*, **31**, 1573 (1898); R. C. Hockett and C. S. Hudson, *J. Am. Chem. Soc.*, **56**, 1632 (1934).

(2) G. Zemplén, *Ber.*, **59**, 1254 (1926); "Organic Syntheses" **20**, 14, 74.

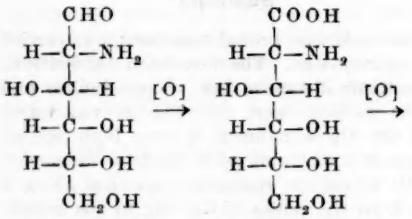
(3) R. A. Weermann, *Rec.*, **37**, 16 (1917); *C. A.*, **12**, 1463 (1918).

(4) H. D. Dakin, *J. Biol. Chem.*, **1**, 171 (1905).

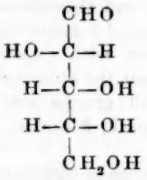
(5) K. Langheld, *Ber.*, **42**, 2360 (1909).

(6) R. M. Herbst, *J Biol. Chem.*, **119**, 85 (1937).

obtained D-arabinose in the form of benzylphenylhydrazone in 20—40% yields. He concludes that the reaction proceeds as below from the fact that the intermediate product, glucosaminic acid, is also oxidized by chloramine-T giving D-arabinose in about 40% yield.

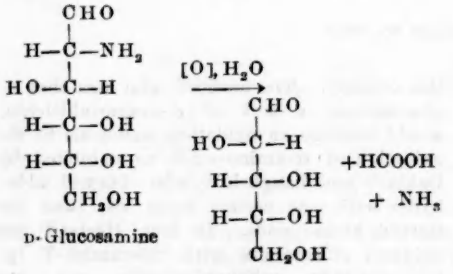


D-Glucosamine D-Glucosaminic acid



D-Arabinose

The author oxidized D-glucosamine with sodium hypochlorite, the amount of which at first being two oxygen-equivalents, assuming that the reaction would proceed as above. Were the mentioned reaction scheme correct, the first carbon atom of glucosaminic acid should be liberated as carbonic acid. But the fact is that D-arabinose is produced in about 30% yield without liberating any carbonic acid. Then, one must conclude that the reaction formulae described above does not represent the fact and a reasonable interpretation of the reaction may be that glucosamine decomposes into arabinose, formic acid and ammonia with one oxygen-equivalent of the oxidant and water as represented below:



D-Glucosamine D-Arabinose

The author's interpretation was confirmed by the experiment in which D-glucosamine was oxidized with one oxygen-equivalent of hypochlorite under ice-water cooling, where D-arabinose-diphenylhydrazone was isolated in a yield above 70% to the theoretical amount. Furthermore, the production of formic acid was confirmed by its reducing action on mercuric chloride and by the analysis of the calcium salt. The application of the method of sugar analysis proposed by Moore and Link[7] revealed also the production of D-arabinose in a yield as high as 75% theoretically. The good yield of the reaction enabled the author to isolate directly crystalline D-arabinose, the yield of the specimen melting at above 150° being round 20% and in the most favourable case 27% yield was secured.

From the results mentioned above it is concluded that glucosamine exhibits a novel type of reaction when oxidized with hypochlorite. It may be worth trying to ascertain that other aminoaldehydes, a type of compound not so familiar to us, have the same character with glucosamine. To this purpose the author took up chondrosamine, a naturally occuring aminoaldehyde, as an example from which it is expected that D-lyxose is formed. The author treated chondrosamine with hypochlorite equivalent to one atom oxygen in the like manner as glucosamine and obtained D-lyxose as its *p*-bromphenydrazone in a yield of 21% to the theory. The formation of formic acid was also confirmed. The low yield of the *p*-bromophenylhydrazone in comparison with the D-arabinose derivative from glucosamine may be due to the incompleteness of the combination of lyxose and *p*-bromophenylhydrazine.

Experimental Part

Preparation of Glucosamine Hydrochloride.— 3 kg. raw dried crab shell is immersed in 20 l. of 2*N*-hydrochloric acid for 3 days with occasional agitation. After washing and drying 1.1 kg. decalcified material is obtained. 500 g. of this material is thrown into 1.5 l. of hydrochloric acid (about 30%) and is heated on a boiling water-bath for 5 hours. To this hydrolysate 1.5 l. water is added and the solution is filtered through Buchner's funnel. The filtrate is concentrated *in vacuo* to about one third of its volume and is placed in a cold room. The colored raw crystals of glucosamine hydrochloride separate and are filtered without washing. The raw crystals are dissolved in as little hot water as possible and are treated with charcoal. The decolorized filtrate is concentrated *in vacuo* until considerable amount of crystals separate which are filtered and washed with a small amount of cold water. The twice

(7) S. Moore and K. P. Link, *J. Biol. Chem.*, **133**, 293 (1940).

repetition of decolorization and concentration of the mother liquor enables above 80% of the raw crystals to be obtained in practically pure state. The yield is 150 g., $[\alpha]_D$ (final), +70.15°.

Oxidation of Glucosamine with Hypochlorite Equivalent to One Atom Oxygen. (a) Isolation of D-Arabinose as its Diphenylhydrazone.—5 g. D-glucosamine hydrochloride is dissolved in 200 cc. water and under ice-water cooling and mechanical stirring the solution of 1 g. sodium hydroxide is added. To this, the solution of sodium hypochlorite is added dropwise at the reaction temperatures below 8°. The oxidation takes place very fast and the reaction is almost completely finished as soon as the oxidant is added. The reaction mixture is neutralized with dilute hydrochloric acid to a weak acid reaction and concentrated *in vacuo* at the temperatures below 40°. The syrup thus obtained is filtered from inorganic salts which have separated during the concentration and the salts are washed with 80% alcohol. A definite portion of the alcoholic solution thus obtained is treated with the alcoholic solution of diphenylhydrazine and the diphenylhydrazone formed of D-arabinose is filtered after over-night standing and washed with 50% alcohol. The crystals melt at 197—198° with decomposition. the yield of which is 73% theoretically to starting D-glucosamine. Recrystallization from alcohol raises the melting point to 198—200° and no melting point depression is observed when mixed with the authentic specimen. Analyses give the following results:

Found: C, 64.88; H, 6.55; N, 8.44.
Calcd. for $C_{17}H_{20}O_4N_2$:
C, 64.54; H, 6.37; N, 8.86.

(b) Analysis of the Oxidation Mixture by the Method of Moore and Link[7].—Using 22.6 g. glucosamine hydrochloride the oxidation is carried out as above. The syrupy product separated from most of the inorganic salts is dissolved in 140 cc. of methanol of which 70 cc. is taken for analysis: 26 g. iodine in 370 cc. methanol is combined with the above methanolic solution of sugar and to this mixture 4% methanolic solution of potassium hydroxide is added dropwise under stirring at 40° until the color of iodine is extinguished. After standing overnight at room temperatures the fine crystals which have separated are collected and washed with methanol. Potassium arabonate thus obtained melts at 210—212° with decomposition and weighs 6.6 g. which corresponds to 62% of theoretical amount to the starting aminosugar. It has a specific rotation $[\alpha]_D^{25}$ − 6.3°. The melting point and the specific rotation given in the literature[7] for the L-isomer is 211° and $[\alpha]_D^{25}$ + 4.5° respectively.

1 g. of potassium arabonate is condensed with o-phenylene-diamine and 0.9 g. arabo-benzimidazole melting at 235° with decomposition is obtained. After recrystallization from 50% alcohol the specimen melts at 237—237.5° and shows no melting point depression when mixed with authentic specimen. The specific rotation $[\alpha]_D^{25}$ is −48.8° in 5% citric acid solution, while $[\alpha]_D^{25}$ given in the literature[7] for the L-isomer is +49.2°. Analysis gives the following results;

Found: C, 55.14; H, 6.00; N, 11.75.
Calcd. for $C_{11}H_{14}O_4N_2$:
C, 55.45; H, 5.92; N, 11.76.

The calculation from the yield of potassium arabonate shows a 75% yield of D-arabinose when one takes account of the empirical factor given in the literature[7].

The distillate of the acidified oxidation mixture gives calcium formate when treated with calcium carbonate in the usual way. The calcium salt in hydrochloric acid solution reduces mercuric chloride to insoluble mercurous chloride and its calcium content is 30.48% while the theoretical value is 30.80%.

Preparation of Crystalline D-Arabinose.—21.6 g. glucosamine hydrochloride dissolved in 100 cc. of water is placed with 200 g. of cracked ice in a beaker surrounded by ice-water. The mixture is then added with 4 g. of sodium hydroxide dissolved in 20 cc. water. Sodium hypochlorite solution (which is prepared by dissolving 7.1 g. of chlorine in a ice-cold solution of 20 g. sodium hydroxide dissolved in 50 cc. water) is run in immediately from the separating funnel under good mechanical stirring. The reaction proceeds smoothly at −3°. After consumption of the oxidant the reaction mixture is neutralized with 6*N*-hydrochloric acid to *p*H 3, and is as far concentrated as possible *in vacuo* at the bath temperature below 45°. The syrup thus obtained is filtered from the considerable amount of inorganic salts and the latter is washed with as little methanol as possible. The methanolic solution of the sugar is again concentrated *in vacuo* and the small amount of salts which have deposited is filtered off. The brown colored thick syrup thus obtained is added with 40 cc. of glacial acetic acid and put in an ice-box. Crystallization takes place shortly. After letting it stand for 2 days the crystal cake is filtered and washed completely with glacial acetic acid. The almost colorless crystals thus obtained weigh 6.7 g. and melt at 127—129°. The raw crystals are dissolved in 4.3 cc. of hot water and then added with 25 cc. of methanol, treated with charcoal, and after seeding put in an ice-box for 2 days. 4.0 g. of D-arabinose meltiug at 150—151° is obtained which is quite free from chlorine ion.

The recrystallized specimen which melts at 155—156° has the specific rotation −103.0° (final) and the following composition:

Found: C, 39.84; H, 7.16.
Calcd. for $C_5H_{10}O_5$: C, 40.00; H, 6.71.

Oxidation of Chondrosamine to D-Lyxose.—Chondrosamine was prepared from the cartilage of shark or from bovine trachea through

chondroitin-sulfuric acid following the methods of Kondo[8], or Fuerth, Bruno, Boyer and Peschek[9] and Levene and La Forge[10]. Chondrosamine hydrochloride obtained was not quite pure though it was a colorless fine crystal.

4.8 g. chondrosamine hydrochloride is dissolved in 100 cc. water and under ice-water cooling and mechanical stirring, 17 cc. of *N*-sodium hydroxide is added. 18 cc. of sodium hypochlorite which is equivalent to one atom oxygen is dropped within the next 10 minutes. After 30 minutes more the reaction mixture is slightly acidified with dilute hydrochloric acid and evaporated *in vacuo* at the temperature below 40°. The distillate contains formic acid. The syrup is freed from inorganic salts and condensed with *p*-bromophenylhydrazine.

The water solution of the syrup is mixed with the alcoholic solution of *p*-bromophenylhydrazine and a small amount of precipitate which is inorganic salts is filtered off after over-night standing. A thick syrup which is obtained by concentrating the filtrate *in vacuo* becomes crystalline when seeded. After letting at stand over-night the crystals are filtered and washed with water to be freed from a syrupy matter. The orange-yellowish crystals thus obtained melt at 148—151° and weigh 1.1 g.

0.5 g. of raw crystals is recrystallized from 30% alcohol. Slightly yellowish needles thus obtained weigh 0.4 g. and melt at 154—155° and show no melting point depression when mixed with the *p*-bromophenylhydrazone of D-lyxose which is prepared from calcium D-galactonate by the Ruff-degradation. Analyses give the following results:

Found: C, 41.01; H, 4.78; N, 8.43.
Calcd. for $C_{11}H_{15}O_4N_2Br$:
C, 41.39; H, 4.74; N, 8.78.

$[\alpha]_D^{28}$ in pyridine in as follows:

Time after solution	$[\alpha]_D^{28}$	$[\alpha]_D$ in the literature[11]
10 min.		+31.8°
15	+33.9°	
60	+27.9	
24 hrs.	+ 9.97	+ 7.8
48		+ 7.8

This paper owes its existence to the apt guidance of Prof. Dr. S. Akabori and industrious assistance of Mr. T. Ikenaka. The author expresses his gratitude to these persons and to Mr. K. Fujino who has kindly sent a large amount of crab shells to the author.

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(8) K. Kondo *Biochem. Z.*, **26**, 116 (1910).
(9) O. Fuerth, T. Bruno, R. Boyer and K. Peschek, *Biochem. Z.*, **294**, 153 (1937).
(10) P. A. Levene and La Forge *J. Biol. Chem.*, **18**, 123 (1914).
(11) P. A. Levene and La Forge, *J. Biol. Chem.*, **18**, 325 (1914).

Conductometric Titration of Cation Exchange Resins

By Tunetaka SASAKI and Ayako INABA

(Received September 25, 1950)

Introduction

There have been various methods to determine the exchange capacities of exchangers, for example, the analysis of the supernatant obtained from the salt solution added in large excess to exchanger[1] or the analysis of the effluent of salt solution coming from a column of exchanger.[2][3] But these methods give no information about the exchange tendency or dissociation degree of exchange groups. The potentiometric method[4][5][6][7] and some other means[8] have also been reported for the determination of the above mentioned quantities. But these are often complex in procedure

(1) H. Jenny, *Kolloid-Beihefte*, **23**, 428 (1939).
(2) R. J. Myers J. W. Eastes and F. J. Myers, *J. Ind. Eng. Chem.*, **33**, 697 (1941).
(3) R. J. Myers and J. W. Eastes, *J. Ind. Eng. Chem.*, **33**, 1203 (1941).
(4) W. C. Bauman and J. Eichorn, *J. Am. Chem. Soc.*, **69**, 2830 (1947).
(5) H. P. Gregor and J. I. Bregman, *J. Am. Chem. Soc.*, **70**, 2370 (1948).
(6) H. G. Cassidy, *J. Am. Chem. Soc.*, **71**, 402 (1949).
(7) I. H. Undegraff and H. G. Cassidy, *J. Am. Chem. Soc.*, **71**, 407 (1949).
(8) E. Heyman and I. J. O'Donnell, *J. Colloid Science*, **4**, 395 (1949).

and the detailed experimental results have not been available for discussion.

The present paper deals with the relatively simple method of conductometry and also with the analysis of its results for the determination of both exchange capacity and tendency of resins.

Experimental

Sample.—The resins used included: (A) Dowex 50; (B) phenoxyacetic acid–formaldehyde; (C) Amberlite IR-C 50; (D) hydroquinone-formaldehyde; (E) phenolsulfonic acid–formaldehyde; (F) sulfonated coal. In these resins each of (A), (B), (C) and (D) had only one kind of exchange group, namely (A) had SO_3H group, (B) and (C) COOH, and (D) phenolic OH. (E) had two kinds of groups, SO_3H and OH, and (F) was supposed to have more than two kinds of groups. (A), (C) and (E) were commercial products and the others were prepared as follows. (B) was prepared by condensation of phenoxyacetic acid and fromaldehyde with hydrochloric acid as catalyst, and (D) by condensation of hydroquinone and formaldehyde with sodium hydroxide as catalyst with the subsequent promotion of the polymerization by heating in each case. (F) was prepared from bituminous coal of Takashima coal mine by treating with hot mixture of conc. sulfuric acid and potassium bichromate with a trace of mercuric sulfate as catalyst. These resins were used as grains of 48~100 mesh size excepting (C) of 20~30 mesh which condition was adopted because this resin was easily ground into very minute particles unsuitable for our purpose. The resins were converted into H-form by rinsing with 2 *N* sulfuric acid solution before using.

Titration.—From one to five g. of swollen resin and 50 cc. of conductivity water were introduced in a 200cc. glass vessel and the whole mixture were titrated with 0.5 *N* sodium hydroxide solution conductometrically. In this process, sodium hydroxide solution was gradually added, one cc. at each time, with constant stirring and conductivity of the supernatant was determined after each addition under the equilibrium condition. Time required to attain the equilibrium was about 5~10 min., although in the case of some resins it became as long as 30 min. in the final stage of titration. To avoid the effect of carbon dioxide, air free from it and saturated with water vapor was passed through the solution during the titration. Moreover suitable corrections were made when the case required.

Results and Discussion

(1) Results of measurements for (A), (B) and (C) resins were shown in Fig. 1. Here x was the adsorption value in terms of eqivalent of sodium ion per 1000 cc. swollen resin and u was the equilibrium concentration of solution in terms of equivalent of sodium ion

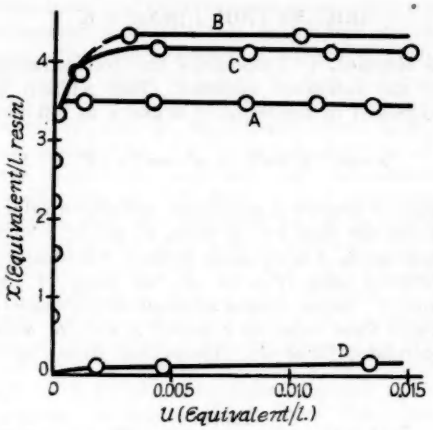

Fig. 1.—Exchange adsorption of NaOH by Dowex 50 (A), phenoxy. resin (B), Amberlite IR-C 50 (C), and hydroquinone resin (D).

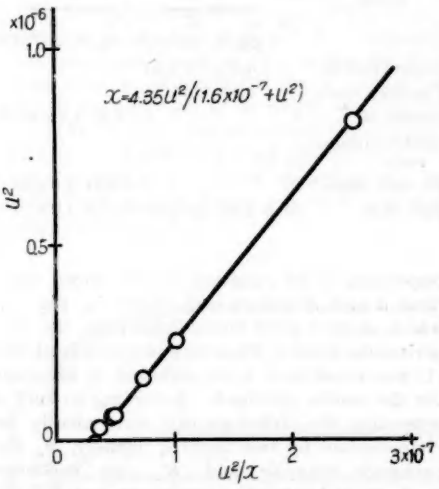

Fig. 2.—Exchange equilibrium for (B) resin.

remaining in 1000 cc. of solution together with resin.

Generally, when the cation exchanger in H-form is treated with sodium hydroxide solution, the equilibrium

$$RH + Na^+ + OH^- \underset{K}{\rightleftharpoons} RNa + H_2O$$

is established. Here RH and RNa represent the exchanger in H-form and Na-form respectively, and K denotes an equilibrium constant. In this case if mass action law is applicable, the relation

$$[RH][Na^+][OH^-]/[RNa] = K$$

is obtained. [ ] represents the concentration of the substance inscribed. This relation is expressed in the terms of u and x as follows:

$$x = au^2/(K+u^2) \text{ or } u^2 = au^2/x - K \qquad (1)$$

Here a denotes a maximum adsorption value. Using the data for (B) resin, u^2 and u^2/x were calculated. A fairly linear relation was obtained between them (Fig. 2). In the cases of (A) and (C) resins, similar relations were obtained. From these relations constant a and K were calculated (Table 1). Theoretical curves corresponding to the equation (1) were drawn using these a and K values (solid lines in Fig. 1), which showed good coincidence with the experimental results. Thus the adsorption isotherm (1) was considered to be sufficient to acccount for the results obtained. According to such a reasoning, the exchanger can conveniently be characterized by two factors, namely, a, the exchange capacity and K, the exchange tendency as has been generally accepted.[4][9][10] In fact, the value of K for (A) resin having SO_3H group is an order of 10^{-11}, while the values are $10^{-7} \sim 10^{-8}$ for (B) and (C) resins both having only COOH group. From these results it is concluded that SO_3H group has a stronger exchange tendency than that of COOH group, which is of course in accord with results obtained by others.[4][5] Fluctuation of the value of K for (B) and (C) resins, both having COOH group, may be ascribed to the difference in molecular structure and degree of gelation of these resins.

Table 1

Exchange Equilibrium Constants of Exchange Groups in Several Exchangers

Resin	Exchange groups: OH	COOH		SO_3H	
	k	a	K	a	K
		eq./l.	eq.²/l.²	eq./l.	eq.²/l.²
Amb. IR-C 50		4.22	2.4×10^{-8}		
Phenoxy. resin		4.35	1.6×10^{-7}		
Dowex 50				3.51	1.2×10^{-11}
Hydroquinone resin	*ca.* 1.7				
Ph. sulf. resin	27			1.34	2.0×10^{-9}
Sulf. coal	51.5	0.27	3.5×10^{-8}	0.75	1.0×10^{-9}

(2) Results obtained for (D) resin was shown in Fig. 1. $u^2 \sim u^2/x$ curve is linear excepting in the region of small u value. In this connection it is worth while to refer to phenol formaldehyde resin. Novolack resin which was prepared by condensation using acid catalyst and showed low polymerization degree, was soluble in alkaline solution and so it was of no ure as an exchanger, while a resin such as Bakelite which was prepared by alkaline catalyst, and which showed high polymerization degree, was insoluble in alkaline solution, but it was again useless as an exchanger because of its no exchange capacity. We can however, expect the existence of the phenol formaldehyde resin having intermediate properties of being insoluble and showing weak exchange tendency. Considering from the results of such a phenol resin and (D) resin, it may be said that OH group of the resin generally shows very weak function, giving large value of K. The value of K may also suffer fluctuation due to the variety in molecular structure of the resin. Such a weak adsorption can conveniently be expressed by $x' = ku$ as shown in gradual increase in x' in the region of large u value in Fig. 1, though the equation (1) rather gives $x = ku^2$ in the case of $K \gg u^2$. It must be noted that the case may not be a mere adsorption, but for the present purpose this is not a matter of importance as the equation $x' = ku$ is sufficicnt to characterize the behavior of phenolic OH group of the resin.

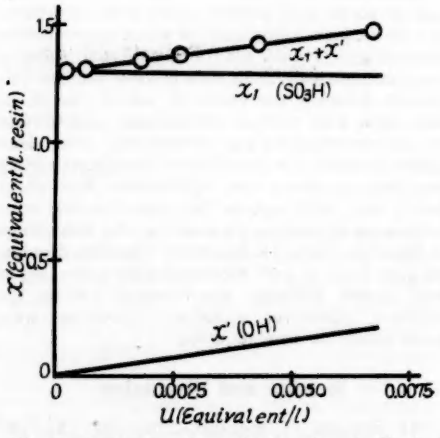

Fig. 3.—Exchange adsorption by phenolsulfonic acid formaldehyde resin (E).

(3) The results of experiments for (E) resin was shown in Fig. 3 (marked with ○). This

(9) M. Honda, *J. Japanese Chem.*, **2**, 386 (1948).
(10) G. E. Boyd, J. Schubert and A. W. Adamson, *J. Am. Chem. Soc.*, **69**, 2818 (1947).

adsorption curve shows steep inclination in the small u region with subsequent and abrupt change in direction which can be interpreted as an existence of a strong exchange group perhaps of SO_3H. After the sudden change in direction, the amount of adsorption still increases gradually and linearly with equilibrium concentration. This gradual increase may be ascribed to the existence of OH group, for which the above equation $x'=ku$ ($k=27$) may be given. Then, the remaining part of adsorption, $x-x'$ may be ascribed to SO_3H group and for this part the value of a and K were determined by the similar method as mentioned above (Table 1). The theoretical curves thus obtained for SO_3H and OH were shown in Fig. 3 (x_1 and x' respectively), the resultant curve (x_1+x') of which fairly coincide with experimental results. It can be concluded from such an analysis of the experimental results, that the (E) resin contains two kinds of exchange groups and no more group of any kind is necessary for the explanation. The value of K for SO_3H of this resin is hundred times greater than that of (A) resin, which is again explained by the difference in structure between these resins as in the case of COOH. We can, however, make clear distinction in order of magnitude of K between SO_3H and COOH.

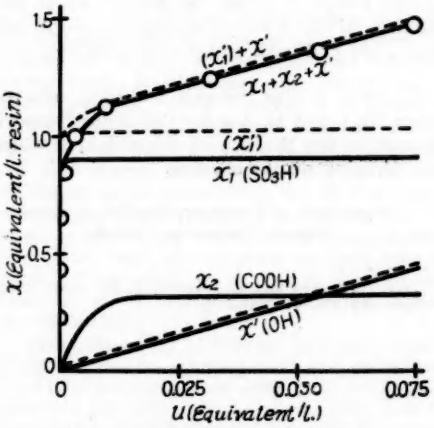

Fig. 4.—Exchange adsorption by sulfonated coal (F).

(4) The results obtained for sulfonated coal (denoted by ○ in Fig. 4) also showed linear increase in adsorption in the region of large equilibrium concentration. From the linear part of this curve we obtained $x'=ku$ ($k=51.5$) for phenolic OH group. Using this value of k, the values of x' and $x-x'$ accordingly were calculated for each concentration. We then attempted to explain this remainder part by supposing only one kind of exchange group. From the values of a and K thus obtained, and also from k for OH group, two adsorption curves (x'_1 and x' respectively) were drawn, the resultant (x'_1+x') of which however did not coincide so well with the experimental results (Fig. 4). Therefore it was considered that at least two kinds of exchange groups other than OH took part in this case. Then, from the initial part of $u^2 \sim u^2/(x-x')$ plot, the constants a_1 and K_1 for stronger group were obtained (Table 1). Using these constants the corresponding adsorption amounts x_1 were calculated by equation (1) and from $u^2 \sim u^2/(x-x'-x_1)$ plot, the constants a_2 and K_2 for another exchange group were determined (Table 1). The adsorption amount (x_2) due to the latter group, was also calculated using a_2 and K_2, and plotted together with x_1 against u (Fig. 4). The resultant x_1+x_2+x' thus obtained plotted against u closely coincided with the experimental results. From such a reasoning it can be concluded that sulfonated coal has two different types of exchange groups in addition to phenolic OH group. These two groups are supposed to be SO_3H and COOH, when we consider the facts that the constant K_1 and K_2 measured fall in the region of the order of magnitude of K estimated in the earlier part of this paper for such exchange groups mentioned.

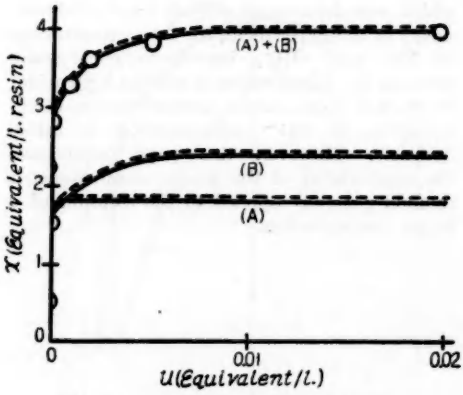

Fig. 5.—Exchange adsorption by a mixture of (A) and (B) resins.

(5) The results of measurement for (A) and (B) resins were shown in Fig. 5. The sum (solid line (A)+(B)) of the each adsorption amount of the two resins (solid lines (A) and (B)) calculated from the constants a and K

Table 2

Exchange Equilibrium Constant of a Mixture of Dowex 50 and Phenoxy. Resin

	Values calcd. from the separate determination	Values calcd. by the analysis of the results for mixed resin
Phenoxy. resin (COOH)	a =2.18 eq./l.	a =2.39
	$K=1.6\times10^{-7}$ eq.^{2}/l.^{2}	$K=1.0\times10^{-7}$
Dowex 50 (SO_3H)	a =1.75	a =1.76
	$K=1.2\times10^{-11}$	$K=3.2\times10^{-10}$

which were previously determined by the separate measurement, agreed well with the experimental results (indicated by circles) for their mixture. The values of a and K obtained by the analysis of the experimental results for the resin mixture and the adsorption curves corresponding to them (dotted lines in Fig. 5) also coincided well with those obtained by the separate determination. These circumstances have some bearing upon the fundamental assumption in the present experiment that the total exchange capacity of an exchanger is the sum of the exchange capacities of each component exchange groups, although the lack of similarity between mechanical mixture of two different types of resins and the mixture of two different exchange groups in molecular scale, still leaves some questions behind.

(6) Finally, we should like further to note a few points. It is inevitable that the basic assumption made for the derivation of equation (1), namely, the substitution of the analytical concentration of sodium hydroxide, which was determined directly from conductometry in this experiment, for the concentrations of Na^+ and OH^-, introduces considerable error in the dilute region of sodium hydroxide. From this point, direct potentiometric determination of OH^- concentration is rather desirable. However, this paper emphasizes the applicability of the simple conductometric method generally applied to the solution of a larger concentration.

Consideration of activity in place of concentration is neglected for simplicity, which must be taken into account for precise discussion.

It has been reported that the dissociation constant of polymer electrolyte should be very complex in character,[11] however, the existence of the mean dissociation constant might still be considered. With the change in molecular structure and the degree of gelation of the resin, mutual effects of exchange groups are affected and the dissociation constant of the groups or the equilibrium constant K fluctuates. However, the fluctuation due to these factors is small compared with that due to the variation in exchange groups. The exchange group can therefore be identified by the value of K.

Summary

Cation exchange resins in H-form each having only one kind of exchange group were titrated with sodium hydroxide solution conductometrically. The results were analysed, and exchange capacity and tendency of each exchange group were determined. A mixture of two resins, each having one kind of exchange group was titrated. The analysis of the results gave adsorption values which agree well with that expected from the determination for the separate resin. From the titration results for more complex cation exchange resins the number of the sorts of exchange groups was estimated and each group was identified.

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(11) I. Kagawa and K. Tsumura, *J. Soc. Chem. Ind., Japan*, **47**, 453, 574 (1944).

Etudes spectroscopiques des complexes métalliques du diphénylthiocarbazone. II[1]

Par Seinosuké MIYAKAWA et Taku UÉMURA

(Reçu le 14 octobre, 1950)

Introduction

Nous avons déjà publié sur les recherches des spectres d'absorption des complexes du diphénylthiocarbazone (dithizone) formés avec l'argent, le cuivre, le zinc, le cadmium, le plomb et le bismuth dans notre mémoire précédent[2]. Le présent compte-rendu inclut une méthode spectrochimique pour déterminer les structures des complexes du dithizone formés avec le cobalt, le nickel et l'or. Le mécanisme d'absorption lumineuse par le dithizone est aussi expliqué dans la publication actuelle.

Procédé expérimental

Nous avons appliqué "la méthode de variation continue" présentée par P. Job[3] pour déterminer la constitution chimique des complexes du diphénylthiocarbazone. En changeant un peu seulment à la fois la quantité d'ion métallique qui forme le complexe, nous pouvons l'extraire avec la quantité définie de la solution normale du dithizone dissous dans le tétrachlorure de carbone et séparer le mélange du complexe dissous avec le dithizone non réactif de la couche aqueuse. Pour mesurer, à ce moment, l'absorption en utilisant une longueur d'onde spéciale, nous avons à choisir la longueur d'onde qui peut donner la variation maxima par la formation du complexe. Au cas du dithizone, sa première bande d'absorption ($\lambda = 620$ mμ), la longueur d'onde qui montre le pouvoir absorbant minimum donné par le point du fond dans la courbe d'absorption et la bande d'absorption produite par le complexe nouvellement formé ont été choisies.

Les réactifs et les dissolvants qui sont utilisés à nos expériences ont été purifiés par les indications déjà montrées dans notre publication précédente. Les sels métalliques employés pour la préparation des complexes sont les trois suivants: sulfate de cobalt dérivé du carbonate de cobalt (marque allemande "Kahlbaum"), acétate de nickel (marque "Kahlbaum") et chloro-aurate de sodium purifié obtenu par la dissolution le fil d'or pur dans l'eau régale. Nous avons préparé la solution aqueuse acide du sel cobaltique et celui du nickel, tous les deux tamponnés par l'acide acétique et l'acétate de sodium en donnant pH = 6.0. Nous étions encore prêts pour la solution aqueuse neutre du sel aurique. Nous nous sommes servis du spectrophotomètre Nutting construit par Hilger et de celui du modèle Spekker et du spectrographe en quartz "type QF-60" construits par Shimazu pour la mesure des bandes d'absorption. Dans nos études actuelles, la concentration du dithizone était 6.28×10^{-5} mol/l. et la longueur du tube d'absorption, 1 cm.

Spectres d'absorption

Nous avons montré dans la Fig. 1 les courbes d'absorption dans la région visible produite par les complexes du dithizone et des résultats numériques dans la table suivante.

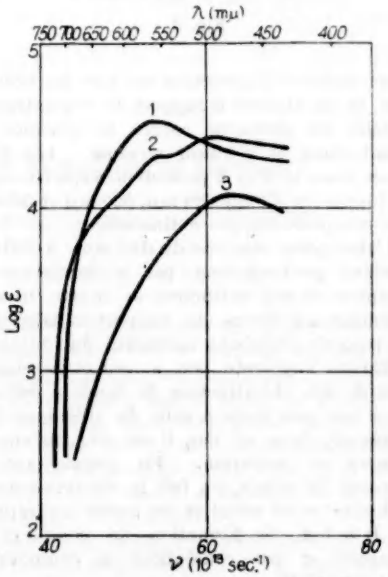


Fig. 1.—Absorption des complexes.
1, CoD_2; 2, NiD_2; 3, AuD.

La Fig. 2 nous expose la variation des extinctions quand les complexes se forment.

(1) Exposé fait lors de la Séance de Tokai-shibu (Nagoya) de la Société chimique du Japon, le 13 novembre, 1949.

(2) T. Uémura et S. Miyakawa, *Bull. Chem. Soc, Japan*, **22**, 115 (1949).

(3) P. Job, *Ann. chim.*, [10], **9**, 113 (1928).

Table

Absorption lumineuse par le dithizone et ses complexes métalliques

Formule chimique	λ, mμ	ν, sec.$^{-1}$	ε
D	620	51.0×10^{13}	3.05×10^{4}
CoD_2	560	53.5	3.52
NiD_2	490	61.3	2.76
AuD	480	62.5	1.24

ε = des coefficients d'extinction moléculaire
D = dithizone λ = longueur d'onde
ν = fréquence

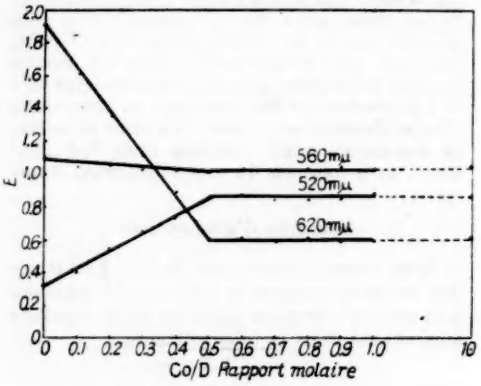


Fig. 2.

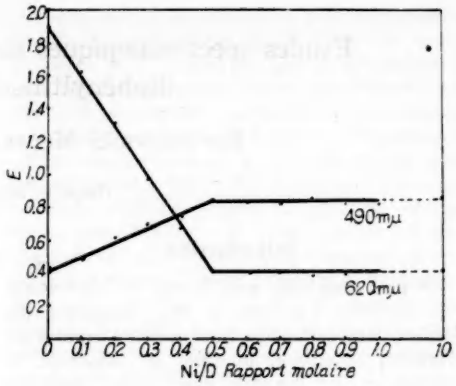


Fig. 3.

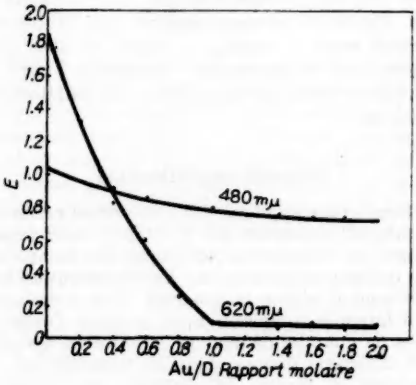


Fig. 4.

Nous mettons l'extinction en axe des ordonnées, et en abscisse le rapport de concentration molaire du dithizone contre la quantité de cobalt dans la solution aqueuse. Les trois lignes dans la Fig. 2 présentent respectivement les longueurs d'onde 620 mμ, 520 mμ et 560mμ que comporte chaque extinction.

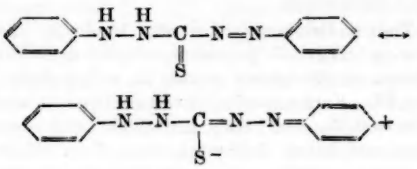
L'absorption maxima du dithizone à 620mμ diminue graduellement par la formation de complexe et son extinction se trouve invariablement au-dessus du rapport molaire 0.5. Le pouvoir absorbant minimum du dithizone à 520 mμ augmente peu à peu et ne change plus de 0.5. L'extinction de bande à 560 mμ est à peu près égale à celle du dithizone lui-même et, dans ce cas, il est très difficile de trouver sa variation. En augmentant la quantité de cobalt, on fait la réaction entre le dithizone et ce métal et on arrive au rapport Co:D = 1:2, la formation du complexe se complète et par conséquent sa composition doit être CoD_2.

La Fig. 3 donne la courbe de réaction entre le dithizone et le nickel. On peut semblablement assigner NiD_2 au sel complexe du nickel. La réaction entre le sel aurique et le dithizone exposée dans la Fig. 4 montre une apparence différente des deux cas précédents. La bande d'absorption du dithizone à 620 mμ diminue rapidement par l'augmentation de la quantité d'or qui indique la valeur définie minima au-dessus du rapport 1. La bande d'absorption du complexe aurique à 480 mμ nous montre, au contraire, une tendance à diminuer au rapport au-dessus de 1, et elle n'a pas de point de détour très clair. Cela nous explique que le AuD formé se change partiellement lorsque le sel aurique augmente. Dans le cas de la formation de AuD_3, le point de détour assez clair doit se trouver au moins à une des deux courbes dans la Fig. 4 à l'endroit rapport molaire 0.33. La décomposition de AuD est donc due à employer une partie de dithizone en dehors de la formation du complexe lorsque le sel aureux est oxydé en sel aurique.

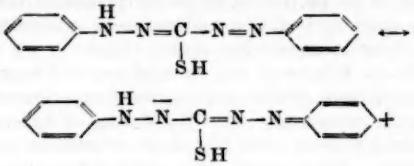
Mécanisme d'absorption lumineuse par le dithizone

Le dithizone cétonique a une bande d'absorp-

tion très intense en région de longueur d'onde élevée (620 mμ) et cette bande déplace en longueur d'onde plus courte en formant le complexe, ce que nous avons déjà exposé dans notre mémoire précédent.[2] Nous supposons que cette bande intense se produit à cause de la liaison S = C <, où le soufre est considérablement électronégatif et a une relation intime avec la résonance suivante.



En formant le complexe, deux électrons émis de l'atome d'azote qui se trouve dans le radical azoique, voisin de celui benzène, s'entremêlent dans la liaison de coordination et la migration de charge électrique indiquée se contrarie. Dans ce cas, la résonance déjà montrée s'affaiblit et la première bande d'absorption du dithizone subira peut-être l'effet hypsochromique. Quant au type énolique, l'effet du soufre contre l'atome du carbone central diminue, et le type dipolaire (constitution droite dans la résonance suivante) exigera probablement une énergie plus élevée.



Par cette raison, on pent prévoir que la première bande d'absorption du composé énolique est remarquablement hypsochromique en comparant celle du type cétonique.

Résumé

(1) Nous avons trouvé les constitutions complexes métalliques (Ni, Co et Au) du dithizone par le procédé spectrochimique.

(2) La première bande d'absorption du dithizone subit l'effet hypsochromique par la formation du complexe ou la production d'isomère énolique. Nous avons expliqué ce résultat expérimental par la constitution résonante.

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The Wet Oxidation and the Structure of Carbon

By Hideo AKAMATU, Hiroshi TAKAHASHI and Kenzi TAMARU

(Received on November 18, 1950)

Introduction

In recent years, the view that the so-called amorphous carbon consists of minute crystallites of graphite has been modified[1] in the strict sense of the word. Most kinds of carbon give the characteristic X-ray powder photographs known as "carbon pattern." This shows that the molecular structure of carbon is made of a layer plane of condensed aromatic rings. However, it is thought that the plane molecules do not arrange themselves in a regular manner as in graphite, namely, it is thought that they are paralleled to each other in layers equally spaced along the *c* axis, but are otherwise disordered along the *a* and *b* axis. Thus, the true three-dimensional atomic lattice as in graphite is not built up in amorphous carbon. Such a structure is called by the term of "turbostratic."

Associating with physico-chemical properties of carbon, measurements of the sizes of their crystallites have been carried out by the X-ray examination. The dimension of the crystallite is the order of 10 ~ 60 Å. along the *a* axis, and 10 ~ 40 Å. along the *c* axis, for most industrial carbon. Now, there remains a problem which must be investigated hereafter;

(1) U. Hofmann and D. Wilm, *Z. Elektrochem.*, **42**, 504 (1936); A. H. White and L. H. Germer, *J. Chem. Phys.*, **9**, 492 (1941); J. Biscoe and B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942); H. Akamatu, *J. Chem. Soc. Japan*, **64**, 1251 (1943); H. Akamatu and K. Nagamatsu, *J. Colloid Science*, **2**, 503 (1947).

that is, in what manner do these crystallite micelles aggregate themselves? For the larger part of the properties, by which types of carbon are characterised, is considered to be attributed to those inter-micellar aggregations.

H. L. Riley and his co-workers,[2] for example, have carried out a series of experiments on the measurements of the change of dimensions of crystallites by heat treatment of carbon. Their results gave much informations about the inner structure of carbon which can not be expressed merely by the statements of the crystallite sizes. We have also carried out a series of experiments on the wet oxidation of carbon, that is, on the reactivity of carbon for the oxidizing solution, and also followed the changes in dimensions of crystallites under the oxidation process by the X-ray examination.

Reactivity to the Wet Oxidation and the Types of Carbon

Carbon is oxidized to carbon dioxide by the solution of potassium dichromate in phosphoric acid. The velocity of this reaction is very slow at the room temperature, but accelerated by moderate heating. It also varies widely depending upon the kind of carbon. This fact can be used to compare the features of carbon with each other.

The oxidizing solution was made by dissolving 20 g. of potassium dichromate into 100 cc. of phosphoric acidd of which density is 1.75. Each experiment was carried out with 0.03 ~ 0.05 g. of carbon, which had been powdered below 140 mesh, and 7 cc. of the oxidizing solution. A small glass vessel containing the reactants was dipped into a water bath at 100°, and then the volume of carbon dioxide produced was measured by a gas

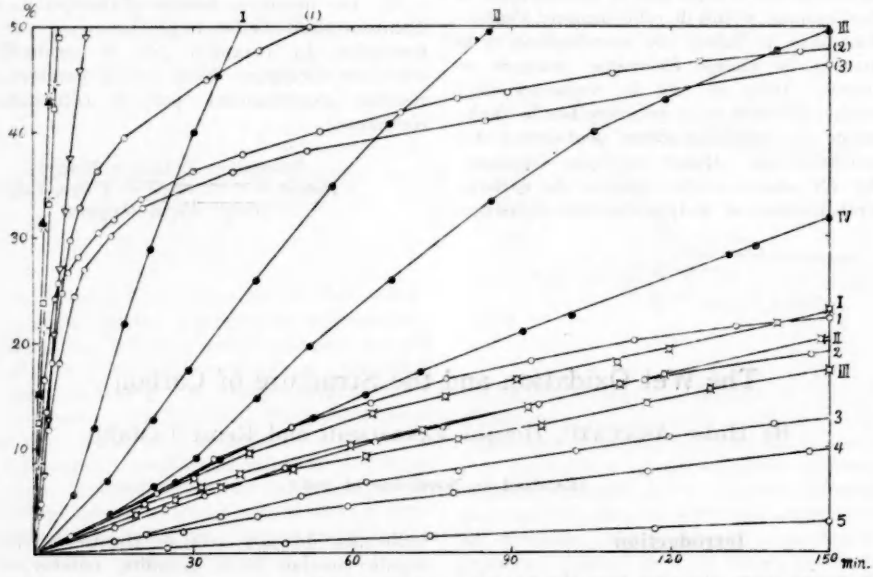

Fig. 1.—The rate of oxidation of various kinds of carbon by the solution of potassium dichromate in phosphoric acid. The fraction of carbon oxidized is shown in percentage against the reaction time in minutes.
Carbon Black: —×—×—, Micronex; —▲—▲—, Tokyo Gas Co.; —□—□—, Nippon Kasei Co.; —+—+—, Nippon Sekiyu Co.; —▽—▽—, acetylene black. Graphite: —●—●—, I, Acheson graphite; II, a natural graphite in Japan; III, flake graphite in Japan; IV, Ceylon graphite. Active carbon: —○—○—; (1), Norit; (2), Active carbon Takeda; (3), Supra-Norit. Pitch coke: —▫—▫—, I, an industrial product in Japan; II, Great Lake; III, an industrial product in Japan. Charcoal: —○—○—, 1, char prepared from filter paper at 390°C.; 2, char prepared from filter paper at 500°C.; 3, wood charcoal; 4, carbonaseous substance prepared from cane sugar and sulfuric acid; 5, carbosaccharose Kahlbaum.

(2) J. Gibson, M. Holohan and H. L. Riley, *J. Chem. Soc.*, **1946**, 456.

burette following the time.

The results are shown in Fig. 1, where the fraction of carbon oxidized are plotted against the time.

The types of carbon which were used in this experiment are as follows. (1) Carbon blacks, containing several kinds of commercial carbon black made in Japan and also "Micronex" made in U. S. A. (2) Active carbons, containing "active carbon Takeda," "Norit" and "Supra-Norit." (3) Charcoals, containing wood charcoal, chars prepared at 390° and 500° from filter paper, and "Carbosaccharose-Kahlbaum." It also contains carbonaseous matter prepared from cane sugar and concentrated sulfuric acid. (4) Pitch cokes, containing commercial products in Japan and U. S. A. (5) Graphites, containing Acheson graphite, Ceylon graphite and two kinds of natural graphite in Japan.

Of all these types of carbon, carbon blacks were oxidized with the highest rate of reaction. Most of them have the same order of the reactivity to the oxidizing solution. The samples of graphite were oxidized with moderate velocities. We can not estimate the crystallite sizes of these samples, because they are all infinitely large under the X-ray scale. However, the curves seem to be arranged in the opposite order of the apparent crystallisation, namely, the velocity of artificial Acheson graphite is the highest and that of Ceylon graphite is the lowest. Between them two kinds of natural graphite in Japan are situated.

The charcoal group has the lowest reactivity to the oxidizing solution, nevertheless the crystallites of these carbons are very small as it is well known. Hence, the fact that they have a large resistance to the wet oxidation, suggests that there must be some important difference in the inner structure between charcoals and carbon blacks. The reactivity of pitch cokes is in the same order as that of charcoals. This suggests that these two kinds of carbon have common characteristics in the inner strucuture.

The curves of active carbons are distinguishable from others by their shapes. At the first part of the reaction, active carbons were oxidized with the velocity as rapidly as carbon blacks were. After 20 ~ 30 per cent of carbon was oxidized, however, the velocity dropped down to the value of charcoals. These activated carbons must not be different substantially from charcoals in their main structures, but it seems, from these results, that they have certain portions of which strucutre and that of carbon black are alike. This is supposed to be attributed to the process by which these carbons were activated.

H. L. Riley assumed,[3] in his paper, that the resistance of carbon to the oxidizing solution is attributed mainly to the presence of the bonding of hydrogen between the layer planes of crystallites, and that the rate of oxidation will be higher as the species is progressively graphitized. In the series of his experiments, however, data on carbon blacks have not been found.

Our results will be interpreted, at least qualitatively, by the following assumptions. The reaction to carbon dioxide proceeds through the formation of intermediate compounds as graphitic oxide, of which structure has been investigated by U. Hofmann.[4] Hence, the first step of the reaction is the entrance of oxygen atoms between the layer planes of crystallites. This is accompanied by the swelling of the crystallite micelles along *c* axis. An effect, caused by the formation of graphitic oxide and the swelling, can be presumed, by which the aggregations of micelles will be destroyed and crystallites will be dispersed into the solution. In reality, in the case of carbon black and graphite, it was found always that carbon was dispersed into the colloidal state in the process of the wet oxidation. In consequence of the dispersion, the surface area of carbon in contact with the oxidizing solution becomes larger, and it will progressively increase as the carbon is made of smaller crystallites. The order of the rate of oxidation from carbon black to Ceylon graphite will be interpreted by this assumption.

In the case of charcoals and pitch cokes, on the other hand, we could not find any dispersion of carbon into the colloidal solution. The small reactivity of these substances to the oxidizing solution will be attributed to the fact that their crystallite micelles seem to be prevented to dispersion. It is further assumed that this restriction is due to the binding of micelles with some cross-linkages between them. These cross-linkages are supposed to be caused by the residual carbon atoms, or some others, which are not completed to the aromatic condensation under the carbonisation process.

The assumption that carbon black is made of independently mobile micelles as in graphite and that charcoal is made of non-mobile micelles bridged to each other with cross-linkages, seems to be plausible when we

(3) H. L. Riley, *Trans. Faraday Soc.*, **34**, 1011(1938); Blaydan and H. L. Riley, *J. Soc. Chem. Ind.*, **54**, 159 T (1935).

(4) U. Hofmann, A. Frenzel and E. Csalán, *Ann. Chem.*, **510**, 1(1934).

remember the origin of these kinds of carbon. Carbon black or soot is prepared from substances of low molecular weight through the gas phase, on the other hand, charcoal or pitch coke is prepared in liquid or solid phase, from materials or at least through certain intermediate substances of high molecular weight.

X-ray Examination of the Oxidizing Process

To get further informations, we carried out the X-ray examination of carbon following the process of the wet oxidation. The results support the assumption described in the preceding section. Experimental procedure was as follows.

By controlling the amount of potassium dichromate in the oxidizing solution, it is able to stop the reaction at any desired step of oxidation, before all the amount of carbon is consumed. Thus, after a part of carbon which is equivalent to the amount of potassium dichromate in the solution disappeared, a certain amount of carbon still remains in the solution. This residual part of carbon was used as the specimen of the X-ray examination, after being purified from salts by repeated decantation with water or by dialysis.

X-ray powder photograhps were made by using a cylindrical camera (radius is 50.4 mm.) and copper-K_α radiation filtered by nickel foil. Powder photographs of carbon consist of diffused bands. By measuring the half-peak widths of the diffraction bands, *i. e.* its width at half the peak intensity, it is possible to know the dimensions of the crystallites. The intensities of the patterns have been found for this purpose from the photographic film using a microphotometer. In this case, however, as the blackening on the photographic film is not simply proportional to the X-ray intensity curve. Several devices have been proposed for the means of this correction. The procedure which was devised by us was as follows. The cover of the photographic film was made of three parts side by side in the X-ray camera, the two parts were covered with aluminium foils differing in thickness to each other, in addition with a paper envelope which was commonly used in all three parts. In consequence, a photograph is divided into three parts such as shown in plate 1.

Plate I.—Powder photograph of pitch coke "Great Lake," 60% oxidized. Photograph is divided into three parts, the intensities at the corresponding points in these parts are in ratio 1:0.625:0.344, theoretically.

From the value of the coefficient of absorption of aluminium, $\mu = 130.3$,[5] and the thickness of the foils used, 0.036 and 0.082 mm. respectively, the relative values of the intensities at the corresponding points in the three parts of a photograph can be known, as in ratio of 1:0.625:0.344. The further procedure is the same as that described by G. P. Thomson,[6] in its principle. The patterns were then microphotometered and groups of densities of the corresponding points on the three parts were tabulated. Each group of densities was plotted with density as ordinate and differences of abscissa equal to $\log 0.625$ and $\log 0.344$ respectively. Each group of points was then shifted parallel to the axis of abscissa until the whole lie on a smooth curve, which gives the relation between the blackening and the logarithm of the relative intensity of X-ray. From this a second curve was drawn giving density against the relative intensity itself. Basing on this curve, the corrected intensity distribution curve was obtained from a microphotometer curve.

For the calculation of the crystallite size from the value of half-peak width (B), the Laue-Brill-Pelzer's formula was used,

$$\eta = 0.0884\left\{B\cos\theta - \frac{1}{B}\left(\frac{\pi r}{R}\right)^2\cos^3\theta\right\}$$

where r and R is the radius of the cylindrical specimen and camera respectively, and θ is half the diffraction angle as defined in the Bragg law. η is a pure number related to the crystallite size by the expression $\eta = \lambda/4\pi ma_l$, where λ is the wave length and ma_l represents the extension of crystallite along the a or c axis in our case. From the (002) diffraction band we can estimate the c-dimension, *i. e.* the average height of layer lattices or of piles of plane molecules, and from the (100) diffraction band, the a-dimension[7] *i. e.* the average diameter of the plane molecules.

In Figs. 2 and 3 the c and a dimensions are shown respectively, plotted against the degree of oxidation which is shown as the fraction of carbon disappeared by the wet oxidation. Each figure shows a process which has been

(5) E. W. Pike, *J. Appl. Phys.*, **12**, 206 (1941).
(6) G. P. Thomson, *Proc. Roy. Soc.*, **A125**, 352 (1929).
(7) If Warren's formula (*Phys. Rev.*, **49**, 693 (1942), $B = 1.84\lambda/L\cos\theta$ where L is the dimension of crystallite, is used for the calculation of the a-dimension, the value becomes larger than that calculated by L. B. P.'s formula in the amount of about 70~90 percent.

followed by crystallite micelles, when a solid disappeared by a chemical reaction.

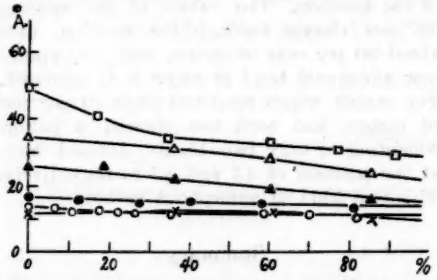

Fig. 2.—The crystallite dimension in Å. along the c-axis is plotted against the fraction of carbon oxidized in percentage.
□, acetylene black; △, pitch coke "Great Lake"; ▲, pitch coke, an industrial product in Japan; ●, carbon black "Miike"; ○, carbon black "Nippon Kasei"; ×, Supra-Norit.

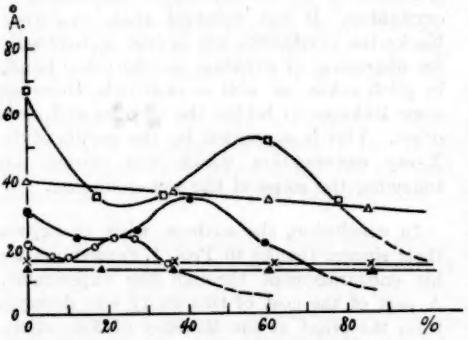

Fig. 3.—The crystallite dimension in Å. along the a-axis is plotted against the fraction of carbon oxidized in percentage. The same symbols as in Fig. 2.

In these figures, changes in the c-dimensions are small all over the degree of oxidation and for all the species of carbon, on the other hand, changes in the a-dimensions are remarkable. Namely, the a-dimension curve of carbon black has a minimum and a maximum. It seems to be a common character of carbon black.

For example, while the first twenty per cent of carbon was lost, the a-dimension of acetylene black decreased from 68 Å. to 35 Å. Such rapid decreasing in the a-dimension will not be expected when we conceive crystallites as small discs and the consumption takes place uniformly along the circumference inward. It is rather logical to assume, from this result, that a disc was split into smaller discs through cracking. Crystallite micelles may contain in their net planes unstable bonds as well as stable bonds. Consequently it is plausible to consider that the reaction proceeds preferentially along weak bonds, and micelles will be split into smaller ones. To interpret the next step, from the minimum to the maximum, it must be remembered that the reaction is an irreversible one, and the growth of crystallite consequently can not be conceived. It must be further remembered that the dimensions measured by the X-ray diffraction method are not other than the average values of the sizes of crystallites, which are even limited to the ordered parts of the micelles, overlooking the disordered parts. The apparent increasing of the a-dimension curve can be attributed to the fact that minute crystallites will be consumed preferentially leaving stable larger micelles behind, in consequence the average values of the dimensions increase. At the maximum point, there remain crystallites with relatively uniform dimensions, and thereafter they are consumed uniformly following the progressive reaction. The results of chemical analysis are shown in Fig. 4. Corresponding to the minimum and the maximum point of the a-dimension curve, there appeared also the minimum and maximum in the oxygen content curve. This supports the above interpretation of the a-dimension curve, because the oxygen content observed can be assumed to be proportional to the total surface of crystallites which can be combined with oxygen.

The behaviors of carbon black can be understood from the assumption that their micelles

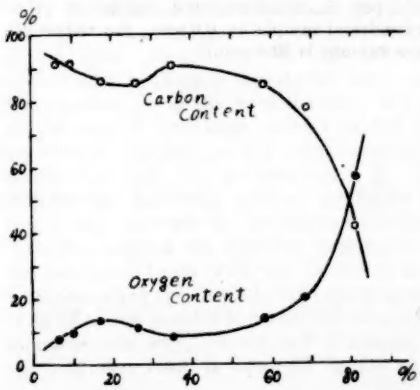

Fig. 4.—Carbon and oxygen content in percentage is plotted against the fraction of carbon oxidized. The sample is carbon black "Nippon Kasei."

are mobile and can be dispersed into the oxidizing solution. Furthermore each micelle can be attacked simultaneously by the oxidizing agent. On the other hand, the *a*-dimension of pitch-coke and Supra-Norit almostly did not change, even when about eighty per cent of carbon had been lost by the reaction. This fact suggests that some micelles at the preferable positions of the total numbers of micelles are consumed preferentially leaving others unchanged, rather than that the total micelles are attacked simultaneously as in the case of carbon black. If the micelles are rigidly bridged with each other to a conglomeration, in which micelles can not move for dispersion and into which the oxidizing solution hardly penetrate, then the micelles being consumed by the reaction are limited to the outer ones of this conglomeration and inner micelles remain unchanged until the outer micelles are completely lost. In consequence, the constancy of the dimensions will be held all over the degree of oxidation.

In Table 1, the observed values of the half-peak widths of (002) and (100) band of Acheson graphite under the process of the wet oxidation are shown. The half-peak widths of the *c*-dimension increased rapidly rather than that of the *a*-dimension. This suggests that the crystallites of graphite split along the layer planes into thinner crystallites in the process of the reaction. The values of the spacings did not change through the reaction, until about 80 per cent of carbon was lost, when a new additional band at about 3 Å. appeared. The sample which remained after 99 per cent of carbon had been lost showed a pattern consisting of only two highly diffused halos at the position of 4.1 and 3.5 Å. respectively. This is a kind of amorphous carbon.

Table 1

The Half-peak Widths of (002) and (100) Band of Acheson Graphite, in the Process of the Wet Oxidation

Fraction of oxidized carbon	0%	25%	50%	80%	98%
	mm.	mm.	mm.	mm.	mm.
(002)	1.25	2.55	2.95	3.15	3.6
(100)	1.35	1.55	1.70	1.85	3.1

(Copper K_α-radiation, the radius of the cylindrical sample is 0.6 mm., the radius of the camera is 50.4 mm.)

Summary

The reactivity of various kinds of carbon to the solution of potassium dichromate in phosphoric acid was examined. The samples investigated contained carbon blacks, graphite, pitch cokes, and charcoals. The rate of the reaction varied depending on the types of carbon, and the order of the reactivity was found to be in the order shown above. This is attributed to the modes of aggregation of crystallites. It was assumed that, in carbon blacks the crystallites are mobile individually for dispersing or swelling, on the other hand, in pitch cokes as well as charcoals there are some linkages to bridge the micelles with each other. This is supported by the results of the X-ray examination which was carried out following the steps of the wet oxidation.

In conclusion, the authors wish to express their sincere thanks to Prof. J. Sameshima for his encouragement through the experiment. A part of the cost of this study was defrayed from the grant of the Ministry of Education, to which the authers' thanks are due.

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Fluorometric Microdetermination of Uranium. IV. Measurement of the Fluorescence Intensity and Determination of the Uranium Content in Natural Substances

By Masaki NAKANISHI

(Received March 9, 1950)

Mesurement of the Fluorescence Intensity

In the way successively described in the foregoing papers, uranium is extracted from the sample in question and mixed with sodium fluoride to prepare the fluorescent material. The prepared fluorescent bead produces a vivid yellow luminescence under the excitation of ultraviolet ray.

This report will recount the particulars in measuring the fluorescence intensity. As shown in the first report of this series, the fluorescence intensity varies with the uranium content of each fluorescent bead, and the larger the content is, the more intense becomes the fluorescence within the range of uranium 10^{-4} to 10^{-9} g.

The bead from an unknown sample is compared on its luminescence intensity with those of known content of uranium, and the uranium content of the former is determined by interpolation.

The high tention mercury lamp was used as the sourse of ultraviolet light, in combination with the glass filter prepared for this purpose.

The measurement is performed, as a rule, with the aid of the photographic spectral photometry, but the visual observation is also often applied expediently.

By the Photographic Spectral Photometry.—As is often available in the measurement of a faint gleam, the photographic spectral photometry is the effective means for measuring the fluorescence intensity.

On the same photographic plate, fluorescence band spectra of both known and unknown beads are photographed in parallel, and the blackness of these bands is compared at the corresponding wave length. In order to avoid the effect of ultraviolet light, which is reflected on the surface of the bead, on the photographic plate, it is necessary to disperse the fluorescence into a spectrum making use of a spectrograph.

Procedures.—The fluorescent bead is supported at a fixed position on the optical axis closely before the widely opened slit of the spectrograph, and is irradiated from a fixed slant direction with the ultraviolet light condensed with a quarz lens of short focus.

As the direction and the position of the discal bead settled in its place affect considerably the density of the photographic plate, they must strictly be fixed.

In order to determine the uranium contents of the unknown beads, the observation of the fluorescence spectra of at least two different known beads are necessary. Spectra of the known and the unknown are taken successively on the same plate, where the time of exposure must be constant for every spectrum, in accordance with the rule of the photographic photometry. The exposure is usually about 10 minutes for the bead containing 10^{-6} g. of uranium, provided that an ordinary panchromatic plate is used. But the time of exposure should be decided by the trial run, for it is subjected to the nature of the plate, as well as the optical system, the intensity of fluorescence and the breadth of the slit.

After the photographing, the plate is developed and the photographic density of each spectrum is estimated at 555 mμ with the microphotometer.

The obtained values of photographic density for known beads are referred to their contents of uranium, and the relation between content and density is established in a convenient way, say, graphically. The particulars of the photographic spectral photometry are omitted here.(1)

By the Visual Observation.—In estimating the intensity of the fluorescence, the photographic photometry has the superiority above other methods, especially for such a faint luminescence as in the present case. But the procedures are somewhat tedious, and if they are faultily followed in any point unexpected results are likely to be obtained. In these respects the following method facilitates the course and provides the satisfactory results.

In this method the intensity comparison of the unknown beads with the known is made with the naked eye, instead of the spectrograph. It is of course possible to make the comparison in the simple way, in which the intensity of the unknown bead is observed in the ultra-

(1) H.B. Dorgelo, *Physik. Z.*, **26**, 756 (1925); R. Frerichs, "Handbuch der Physik", Berlin, 1928, Vol. 19, Chapter 23.

violet light and compared with those of several known beads containing different quantities of uranium. But more accurate results are expected by the following device based on the same principle.

Procedures.—The colorimeter of the Duboscq type is used for this purpose for the sake of convenience. Any turbid solution of an arbitrary concentration is applied to the absorbing layer in the vertical cylinders. Just under each cylinder the fluorescent bead is placed severally. In the one position under one cylinder an arbitrary bead for comparison is settled and kept fixed during the process, and in the other position known and unknown beads are placed one after another. These two beads are compared by the balancing method in the ultraviolet light.

As the fluorescence is in general fairly faint, the microscopic part of the colorimeter is removed to eliminate the absorption and to make the loss of light due to magnification minimum. The fluorescent beads are arranged in such a way that those two images are observed side by side in the scope.

The uranium content in the bead in question is determined as follows.

According to the absorption law of light, the intensity I of the fluorescence in question after passing through the layer d of the turbid solution is given by

$$I = I_0 e^{-kd'},$$

where I_0 and k represent the initial intensity and the absorption constant respectively.

On the other hand, we obtain a similar equation for an arbitrary bead for comparison,

$$I' = I_0' e^{-kd'},$$

where each figure has the corresponding meaning.

When the apparent intensities of both images come equal,

$$I = I'$$

or $$I_0 e^{-kd} = I_0' e^{-kd'}$$

therfore $$I_0 = I_0' e^{-k(d'-d)}.$$

To obtain the values of the two unknown constants, I_0' and k, more than two beads containing different amounts of uranium are compared on their luminescence intensity with the arbitrary bead for the comparison in the manner as given above. Then the uranium content of an unknown bead is obtained from these values of constants in the same procedure.

The above calculation is valid only within the range in which the fluorescence intensity is linearly proportional to the content of uranium of the bead.

This visual observation method has the advantages, in spite of its simplicity, over the photographic photometry in several points. The latter method is not free from imperfections for the purpose of this kind in the following points.

(a) The fluorescence is too faint to make an image on the photographic plate in case the content of uranium is small. In consequence, the time of exposure must necessarily be prolonged. Meanwhile the bead may be wet by the atmospheric moisture especially in the damp weather, and consequently the fluorescence intensity is likely made feeble.

(b) The procedures following after the photographing, e.g., the development of the plate and the measurement of the photographic density, are not easy.

(c) Each operation is subjected to the influences of many factors, and this presumably makes the possibility of the experimental error much.

The visual observation method overcomes these difficulties for all the simplicity in comparison with the photographic photometry. The writer therefore takes the former from his experiences for a suitable method in routine works, and he has got the satisfactory results by the method.

Determination of the Uranium Content in Natural Substances

On the uranium contents of various natural substances which are not regarded as radioactive, almost no direct determination has been carried out so far in this country. Since these nonradioactive substances usually contain such an amount of uranium as is most suitably determined by the fluorometric method, this procedure must furnish the useful means to manifest the geochemical circumstances of radioactive elements.

In dealing with rocks in which uranium is expected to be in the state of equilibrium with radium, the amount of the former is easily estimated indirectly from that of the latter.

The microdetermination of uranium is necessary, especially for the samples in which radioactive elements of the uranium series do not yet reach their equilibrium condition. In these circumstances the fluorometric method is an effective measure.

Included among these are samples from the hydrosphere as well as the biosphere. Furthermore some minerals of which ages are less than a million years from their formation, weathered minerals or rocks, etc. must be treated in the direct microdetermination method to determine

uranium, because uranium is not expected to be in equilibrium with the disintegration products. The following sections will deal with some examples of natural substances treated with the fluorometric method of analysis.

The Uranium Contents of Rocks

Experiment.—The particulars of the treatment are omitted here, for the full description of the analytical procedures appeared in the previous papers.

About 1 g. of the sample suffices for the analysis. In case the sample is first fused with sodium carbonate and leached with hot water as recommended from the writer's experiences, the procedure must be repeated at least three times to make the complete extraction of uranium.

The leached solution containing a considerable amount of sodium carbonate is made acid with hydrochloric acid and evaporated to dryness. From this residue remove silica in the usual way, and to the resulting solution add a little ferric chloride (corresponding to about 20 mg. Fe_2O_3) and ammonium chloride. Boil the solution, make it ammoniacal, continue the boiling for a few minutes, and then filter the precipitate. The filtrate is treated two times more in the same way repeating the precipitation. The first precipitate generally contains some aluminum hydroxide.

Three precipitates are brought together. The combined mass must necessarily be reprecipitated, for it includes much impurities, especially sodium chloride derived from the mother liquor.

The obtained precipitate of iron hydroxide contains the total amount of uranium in the original sample. The after treatments run in the same way as already described.

The interferences of impurities are satisfactorily avoided even in such a normal course of procedures, so far as the common igneous rocks are concerned.

The results obtained on some examples of the rock are listed in Table 1.

Table 1

No.	Sample	Location	Uranium content, 10^{-6} g.U/g.
(1)	Sinter deposit (ferruginous)	Masutomi (Yamanashi Prefecture)	0.05
(2)	Sinter deposit (calcareous)	〃	0.004
(3)	Greywacke	〃	2.15 2.06
(4)	Shale (average sample)	Europe	0.67

The first sample (1) shows the uranium content of the sinter deposit at one of the chalybeate mineral springs in Masutomi district (Yamanashi Prefecture), which is widely known as one of the strongest radioactive spring regions in Japan.

The spring A 8 (as named by earlier investigators),[2] from which the ferruginous sinter grew, is very radioactive owing to its large contents of radium and radon, but the uranium content of the spring water itself (0.3×10^{-6} g.U/g.) is not so large as expected. A part of the dissolved uranium in the spring water must be coprecipitated with iron near the orifice, but the larger part of the element is likely to remain in the solution, because the spring water contains some noticeable amount of carbonate.

The sample (2) is an example of calcareous sinter deposits formed from mineral waters of old times. It consists mainly of calcium carbonate. This sample was obtained in October, 1936, by Dr. Toshio Nakai, who found in it the extraordinarily large content of radium amounting to 1.75×10^{-10} g.Ra/g.[3] The writer is much obliged to him for affording facilities to make use of the sample.

As the result of analysis a very small amount of uranium was found as given in Table 1. If uranium be present to the equilibrium amount to radium, the content would reach 5.15×10^{-4} g.U/g. On the contrary, however, the observed value of uranium is 10^5 times smaller than the expected. This fact shows that uranium and radium are brought into the sinter deposits independently to each other by different mechanisms. Further, it would be natural that uranium does not behave in the same manner as calcium, when considered that uranium forms a soluble complex salt with carbonate. The uranium found in the calcareous sinter deposit will presumably have originated from the permeating mineral water.

The analysis of the sample (3) was attempted to know the uranium content of the ground, from which the strong radioactive springs arise. The sample was taken at the spot between B and C areas[2] of Masutomi district.

The sample (4) is an average sample of various European shales, which the writer received by courtesy of Professor Eiichi Minami. The value obtained corresponds to that of mean basic igneous rocks.

Summary

Details of the methods of measuring the relative intensity of the fluorescence were described, in which the photographic spectral photometry and the visual observation method were related.

(2) S. Osna and K. Kuroda, this Bulletin, **17**, 400 (1942).
(3) T. Nakai, this Bulletin, **15**, 420 (1940).

Several examples of uranium contents in rocks and sinter deposits determined by this method are treated from the geochemical interest.

The writer's thanks are due to Professor Kenjiro Kimura of the University of Tokyo for his continual advice and encouragement in the course of this study.

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Fluorometric Microdetermination of Uranium. V. The Uranium Content of Sea Water

By Masaki NAKANISHI

(Received March 9, 1950)

Experimental

A sample of 200 ml. of sea water is enough to determine the uranium content by the present fluorometric method.

The sample water is treated in the way as described in the foregoing papers. For fear that the organic substances are present in the original sample, the residue of the first evaporation is dealt with nitric acid and evaporated again. Then the residue is dissolved in dilute hydrochloric acid and the insoluble matters are separated.

The iron hydroxide precipitate obtained as the carrier of uranium must be re-precipitated, because it probably includes a certain amount of sodium chloride.

Even in the case when the treatments are carried out along the normal course as given before, almost no noticeable interference of impurities comes about. Consequently no special procedures of removing impurities are required in the analysis of sea water. For this reason the particulars of the processes are omitted here to avoid the repetition.

Results

The uranium content of sea water obtained in several samples are given in Table 1 and 2.

Table 1

No.	Location	Depth, m.	Content of U, 10^{-6}g./l.	Salinity, ‰
(1)	Mutsu-wan (Aomori Prefecture)	0	0.46	28.8
(2)	Sagami-nada (Shizuoka Prefecture)	29	1.36, 1.04 1.20, 1.30 1.06, 1.12 mean: 1.18	34.7

Table 2

	(3) 32°39.1′ N 135°27.0′ E		(4) 31°49.0′ N 135°23.7′ E	
Depth, m.	Content of U, 10^{-6}g./l.	Salinity, ‰	Content of U, 10^{-6}g./l.	Salinity, ‰
0	—	—	1.96	34.72
500	3.37	34.33	2.98	34.61
1000	2.65	34.31	—	—
1500	2.76	34.40	2.55	34.54
2000	2.79	34.52	2.44	34.58
3000	3.06	34.60	—	—
4000	2.70	34.61	—	—

	(5) 31°50.0′ N 133°08.2′ E	
Depth, m.	Content of U, 10^{-6} g./l.	Salinity, ‰
0	1.75	34.45

The sample (1) was taken from the surface water in Mutsu Bay one kilometer off Asamushi (Aomori Prefecture) on April 27, 1946, and the determination was carried out several weeks after the sampling.

The sample (2) was obtained at the mouth of Ito Bay (eastern side of the Izu Peninsula, Shizuoka Prefecture) at the depth of 29 m. from the surface, close to the sea-bottom. This was sampled on April 29, 1947, and the treatment followed soon after.

The samples (3), (4) and (5) were examined in the attempt to find the uranium content of the ocean water, which is less affected by the influences of land. For using these materials as analytical samples the present writer is much obliged to the Hydrographical Department, Ministry of Transportation. Sampling was performed on December 5, 1947, and the treatment came off in June (1948), in

January (1949) and in June (1949) for the sample (3), (4) and (5) respectively. All these samples were kept preserved in the glass bottles.

Discussion

On the uranium content of sea water several reports have been published in foreign countries. Among them Hernegger and Karlik[1] first applied the fluorometric method to this purpose. The results they obtained are given in Table 3.

Table 3

Location	Depth, m.	Content of U, 10^{-6} g./l.	Salinity, ‰
Gullmar Fjord	0	0.36	23.9
〃	60	0.98	34.1
〃	100	1.17	34.3
Skagerak	500	1.90	35.2

The sample water for analysis was taken near the western coast of Sweden. According to their later report,[2] they obtained the values from 2.0 to 2.2×10^{-6} g.U per l. for the uranium content of coast and ocean water.

Later ol Föyn and others[3] reported 1.5×10^{-6} g./l., and this value was approved by Wattenberg.[4]

The present writer intends to compare his results with those given in Table 3.

The sample (1) taken from the surface water close to the coast of a bay is an example of those which are much affected by the inland water. Therefore it is of little importance from the geochemical point of view to discuss in detail on the uranium content of sea water from this result. In this sample of sea water, the uranium content was found to be considerably small just as it was expected, and in the same degree of magnitude as reported previously by Hernegger (Table 3). The only conclusion is that the uranium content will probably be higher in sea water than in common inland water.

Similarly the sample (2) was subject to the influences of land, though a less degree, and can not be looked on as the typical sea water. But the result obtained from this sample shows a fairly large value, which nearly corresponds to that of Hernegger's which was collected at 100 m. depth. In the present case the depth (29 m.) of sampling is of no great importance, because it is also the depth of the sea-bottom. The value obtained will be equivalent to that of the deeper layer of the open sea.

Quite different from these two, the samples (3), (4) and (5) are the true sea water, belonging to the Kuroshio Current, and are supposed to give the uranium content of sea water in various depths.

In these samples the values obtained are in general somewhat larger than expected, except that taken at the depth of 0 m. (surface). The blank test was carried out and the standard fluorescent beads of known content were examined on the correctness. Moreover the relatively high values obtained above are not attributed to the substance contaminated from the glass bottles, though Hoffmann[5] told about the unexpectedly large uranium content of some sorts of glass and porcelain. This is because the uranium in the sample (4), which was treated about half a year later after the sample (3) had been treated, shows no increase in content during the interval.

The concentration of uranium in the surface water is evidently lower than that in the deeper layer. In order to search into the biological concentration of this element, the sample (5) was first filtered through a filter paper, and the remaining residue was ignited to ash. Then the ash was treated by the fluorometric method. But no trace of uranium was found in it, and this fact means that the remains of the dead micro-organisms stayed by the filter paper do not play any important part to concentrate the element. The smaller value in the sample (5) is also consistent with that of the sample (4), though the reason why the sea water is poorer in uranium in the surface layer is not yet finally given.

Even though there comes out a peak at the depth of 500 m., the uranium content of deeper layers seems to be approximately constant, as the determination method involves the error amounting to 10%. Provided that uranium finds itself in the same concentration throughout the deeper layers, the average value comes up to 2.82×10^{-6} g.U/l., and this is the most probable value for the deep ocean water.

This result will be contributive to the problem of the radioactive elements in sea water.

Evans and others[6] made an investigation

(1) F. Hernegger and B. Karlik, *Sitz. Akad. Wiss. Wien*, Abt. IIa, **144**, 217 (1935).
(2) F. Hernegger and B. Karlik, *Göteborgs K. Vetensk-Samh. Handl.*, V. B. 4, No. 12.
(3) E. Föyn, B. Karlik, H. Petterson and E. Rona, *Medd. Oceanogr. Inst. Göteborg*, Nr. 2, (1939).
(4) H. Wattenberg, *Z. anorg. allgem. Chem.*, **251**, 86 (1943).
(5) J. Hoffmann, *Sprechsaal*, **75**, 214 (1942).
(6) R. D. Evans, A. F. Kip and E. G. Moberg, *Am. J. Sci.*, **36**, 241 (1938).

on the radium content of sea water at the western coast of North America, and gave the information of the variation in depth shown in the first column in Table 4.

Table 4

Depth, m.	(I) Content of Ra, 10^{-12} g./l.	(II) Equilibrium amount of U (calc.), 10^{-6} g./l.	(III) U (obs.) / U (calc.) (approximate)
0	0.3 ± 0.1	0.09	20
600	1.5 ± 0.1	0.44	7
1300	3.2 ± 0.2	0.94	3

The amount of uranium which is in the radioactive equilibrium to radium is calculated in the second column. And the last column represents the ratios of the observed values given in Table 2 to the corresponding calculated values. As shown clearly in the table the ratios rapidly decrease with the depth; in other words, it is obviously sure that radium is gradually precipitated in some mechanism,[7] for the concentration of uranium is approximately constant to the depth.

In regard to the thorium content of sea water, several reports have been published, among which the values $<2\gamma$/l.[8], $\leqq 0.5\gamma$/l.[9], 0.5γ/l.[4] and 0.66γ/l.[10] were displayed. The last one was determined with the surface water of the Seto Inland Sea, and this is no more than one third of the corresponding uranium amount. Therefore the relation between uranium and thorium in sea water is in direct opposition to that in common igneous rocks.

Other investigations of the writer show that the largest uranium content of the inland waters ever found in Japan belongs to the water of Shin-arima hot spring (Hyogo Prefecture) amounting to 0.95×10^{-6} g.U/l., which has also the largest content of radium (381.14×10^{-12} g. Ra/l.).

Simple springs generally have less contents, for example, less than 2×10^{-9} g.U/l. for Shuzenji hot spring (Shizuoka Prefecture).

Even Masutomi springs (Yamanashi Prefecture), which are told to be the most radioactive spring group in this country, contain rather a small amount of uranium, that is, from 0.4 to 0.04×10^{-6} g.U/l. as far as the writer has examined.

He also failed to find any noticeable amount of uranium in the analyses of some sorts of river and underground waters.

Although we have received some papers[11] from abroad reporting of finding more uranium in some mineral springs than in sea water, we may conclusively maintain that the sea water in generel has the greatest concentration of uranium in the hydrosphere.

Summary

Coast and ocean water sample were analysed on their uranium contents by the fluorometric method.

The variation to the depth of 4000 m. was also examined in the ocean water sample. The content is likely to be constant even to the deep, though a little decrease appears in the surface water.

The obtained values in the deeper layer (average 2.8×10^{-6} g.U/l.) are somewhat higher than those by foreign investigators.

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(7) C. S. Piggot and Wm. D. Urry, *Am. J. Sci.*, **239**. 81 (1941); H. Hamaguchi, *J. Chem. Soc. Japan*, **62**. 839, (1941).
(8) H. Wattenberg, *Z. anorg. allgem. Chem.*, **236**. 339 (1938).
(9) E. Föyn, D. Karlik, H. Petterson and E. Rona, *Nature*, **143** 275 (1939).
(10) M. Ishibashi and S. Azuma, *Chemistry and Chemical Industry*, **2**, 14 (1949).
(11) J. Hoffman, *Monatsh.*, **74**, 38 (1941).

Studies on the Separation of Arsenic from Iron by Ion-Exchange Resin

By Yukichi YOSHINO

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Although arsenic is an amphoteric element, it has been said that aqueous or dilute hydrochloric acid solution contains arsenic as arseneous or arsenic acid. For the purpose of separating arsenic from iron using cation-exchange resin, the author has made a series of fundamental experiments. It was proved that the trivalent arsenic could be separated quantitatively from ferrous iron, while the separation of quinquevalent arsenic from ferric iron, though theoretically possible, was unpracticable, which seemed perhaps due to the formation of unstable ferric-arseno complex. As an example of practical applications of the method, the content of arsenic as well as iron and sulfur in an arsenopyrite was determined using ion-exchange resin. The results obtained agreed with those of hydrogen sulfide method of separation.

Experimental

The Resin: Cation-exchanger of commercial phenolsulfonic acid type. Ten grams of 30 meshed resin was conveniently equipped in a 50 cc. burette. The flow method was adopted and the rate of flow was 2—3 cc. per minute throughout the experiments. The exchange capacity of the resin was 1.84 milliequivalents per gram with respect to hydrogen ion.

Experiment 1. The Behavior of Arsenic Solution in Passing through the Column of Resin.— The resin was previously saturated with 1*N*-sodium chloride or 1*N*-hydrochloric acid and washed thoroughly with distilled water. Various amounts of standard solutions of arseneous and arsenic acid respectively were added to the column of resin. The filtrate and washing water were received in a measuring flask of 150 or 250 cc. of capacity and the flask was filled up to the mark. The aliquot portions of the filtrate were taken and the amount of arsenic was determined iodometrically as follows:

In case of arseneous acid: The sample solution is neutralized with an excess of sodium bicarbonate and then titrated with 0.01*N*-iodine solution using starch as an indicator.

In case of arsenic acid: The method of determination of arsenic acid[1] is just the reverse of the case of arseneous acid, that is, an excess of potassium iodide is added to the strongly acid solution of quinquevalent arsenic and liberated iodine is titrated with 0.01*N*-sodium thiosulfate solution. In this case, however, the strong acidity of the sample solution is apt to promote the decomposition of potassium iodide and to give the intermediate pink color at the end point of titration. Therefore, special cautions were taken as follows.

Concentrated hydrochloric acid and distilled water are previously boiled and freed from chlorine and air. To ten cc. of the sample solution, add concentrated hydrochloric acid so as to give 6*N* with respect to acidity. Throughout the procedure, a stream of carbon dioxide is led to the solution. Add 1 g. of solid potassium iodide and keep it on standing for five minutes. The liberated iodine is titrated with 0.01*N*-sodium thiosulfate solution. When the end point is near, the solution is diluted with water to 2*N* of acidity and 5 drops of 0.5 per cent starch solution is added and titration is carried out to the end point indicated by the change of color from blue to pink. Using this procedure, the blank value can be kept within 1 or 2 drops in every titration.

The results of such experiments are given in Table 1.

Table 1

Titrated Values of Arsenic after Passing through the Column of Resin

	No. of Expts.	*p*H	Amts. of arsenic, mg. As taken	found	Error, %	Remarks
AsO_3---	1	2.4	93.64	93.57	−0.07	Na-R* → 250 cc.**
	2	1.8	56.18	55.91	−0.51	Na-R → 150 cc.
	3	1.8	56.18	56.29	+0.20	H-R → 250 cc.
AsO_4---	4	1.8	102.0	101.8	−0.20	Na-R → 250 cc.
	5	≦1.0	102.0	100.8	−1.18	Na-R → 250 cc.
	6	1.4	102.0	102.4	+0.39	H-R → 250 cc.

* Na-R and H-R show the types of resin saturated with Na^+ or H^+ respectively.
** Total volume of effluent.

Table 1 shows that both trivalent and quinquevalent arsenic can be passed out through the bed without any loss. Moreover their behavior seems to be independent of the types of resin (Na-R or H-R). These results may enable us to

(1) L. Rosenthaler, *Z. anal. Chem.*, **45**, 596 (1906); **61**, 222 (1922); I. M. Kolthoff, *Z. anal. Chem.*, **60**, 393 (1921); **62**, 137 (1923).

conclude that arsenic of both valency in the dilute hydrochloric acid solution can be treated as anions.

Experiment II. Separation of Arseneous Acid from Ferrous Iron.—The mixed solution of various amounts of arseneous acid and ferrous ammonium sulfate solution was flowed into the column of resin and the filtrate and washing water were collected and made up to a definite volume, say 250 cc., aliquot portions of which were taken and arseneous acid was determined by titrating with 0.01*N*-iodine solution. Distilled water of 100 to 150 cc. was proved to be sufficient for washing. The test of iron in the effluent with dimethylglyoxime or ammonium thiocyanate revealed no reaction at all.

These results show that arseneous acid could be quantitatively separated from ferrous ion as is given in Table 2.

Table 2

Separation of Arseneous Acid from Ferrous Iron

No. of Expts.	*p*H	Iron added, mg. Fe	AsO_3--- taken, mg. As	AsO_3--- found, mg. As	Error, %
1	<1	94.69	18.73	18.60	−0.69
2	1.9	59.53	37.46	37.58	+0.32
3	0.9	59.53	37.46	37.31	−0.30

Experiment III. Separation of Arsenic Acid from Ferric Iron.—A mixture of ferric chloride (94.41 mg. as Fe) and arsenic acid (100 mg. as As) was poured into the column of resin and, to prevent the formation of ferric arsenate precipitate, washed with 0.01*N*-hydrochloric acid solution. But, in this case, the amount of arsenic found in 250 cc. of effluent was about 80 per cent of that originally present. Snccessive washing with distilled water showed the gradual flowing-out of arsenic remained in the column. Table 3 gives the amounts of arsenic found in the filtrate at each step of washing.

About 2000 cc. of water was necessary for washing until the filtrate ceased to show blue coloration with ammonium molybdate reagent.(2)

Table 3

Relation between the Volume of Washing Water and the Amount of Arsenic Found in the Filtrate

cc. of washing water	~250	250 ~500	500 ~750	750 ~1000
AsO_4---found, %	80.33	15.84	2.25	1.31

cc. of washing water	1000 ~1250	1250 ~1500	1500 ~2000	Total As found
AsO_4---found, %	0.13*	0.01*	0.01*	99.88

* determined colorimetricaly with "molybdenum blue" method.

The amount of iron in the filtrate when tested by means of ammonium thiocyanate in the dilute nitric acid medium proved to be trace amount. Between *p*H 0.9 and 2.0, a number of experiments was made varying mixing ratio Fe/As, flow rate and the types of resin (H-R, Na-R or NH_4-R)., but none of them proved to be effective for complete separation of arsenic acid from ferric ion. These results seem to suggest that such behavior of arsenic acid might be attributed to some interaction between ferric ion and arsenic acid.

To clarify the state of affairs, following experiment was carried out. Into the column of 5 g. of resin which was previously saturated with ferric ion, a definite amount of arsenic acid (30 mg. as As) was poured. The filtrate and washing water were collected to a definite volume. The arsenic found in the effluent was 71.8 and 81.3 per cent respectively when the volume of the latter reached to 550 cc. and 1050 cc. On the other hand, a little iron (about a few mg. of ferric ion) was found in the filtrate.

In contrast to above mentioned case, when 56.18 mg. (as As) of arseneous acid passed through the column of 5 g. of resin which was previously saturated with ferric ion, the amount of arseneous acid in 150 cc. of filtrate was found to the extent of 98.2 per cent.

We may hereby conclude that a part of arsenic acid might form some complex ion(3) with ferric iron in the solution. But owing to the relatively weak linkage, the complex ion is gradually dissociated along with the adsorption of ferric ion by the resin and consequently the flowing-out of arsenic acid takes place.

Even in case of oxidized state of arsenic and iron, it was shown that the separation of arsenic from ferric ion was possible when treated previously with sulfur dioxide. The process is as follows. The solution containing both ferric ion and arsenic acid, after being reduced by leading a stream of sulfur dioxide, is poured into the column of resin. The filtrate and washing water are collected to a definite volume, an aliquot portion of which is oxidized with bromine water. The excess of the latter is expelled by heating.

When cooled, 1 g. of potassium iodide is added and the liberated iodine is titrated with 0.01*N*-sodium thiosulfate solution as mentioned in Experiment I. Table 4 gives the results of such experiments.

Table 4

Separation of Arsenic Acid from Ferric Ion after Reducing with Sulfur Dioxide

Fe^{+++} added, mg. Fe	Amts. of arsenic acid, mg. As taken	found	Error, mg. As
94.4	102.0	102.3	0.3
94.4	15.3	15.7	0.4

(2) Denigès, *Compt. rend.*, **171**, 802 (1920); Emill Trug and A. H. Meyer, *Ind. Eng. Chem., Anal. Ed.*, **1**. 136 (1929).

(3) L, Dede, *Z. anorg. Chem.*, **125**, 28 (1922).

Analysis of Arsenopyrite using Ion-Exchange Resin.—As mentioned above, the separation of arseneous acid from ferrous ion is quantitatively carried out. As an example of practical applications, the analysis of an arsenopyrits[4] was tried using ion-exchange resin.

About 0.7 g. of fine powdered sample is weighed out and transfered into a casserol. After digesting with 5 cc. of conc. nitric acid, 5 cc. of bromine is added in portions, while the solution is warmed on a water-bath. When all the sulfur is converted to sulfate, 5 cc. of conc. hydrochloric acid is added and dried up. This is repeated once more. Then, the residue is treated with a small volume of dilute hydrochloric acid and water. The insoluble matter and silica are filtered off. The filtrate is made up to 100 cc.

Determination of Arsenic: An aliquot portion of the sample solution, say 20 cc., is taken and treated with sulfur dioxide. The same procedure as mentioned in the preceeding paragraph is adopted.

Determination of Iron: The adsorbed iron is eluted out with about 100 cc. of 4*N*-hydrochloric acid. The elute is evaporated to a small volume, to which a few drops of 1 per cent potassium permanganate solution are added. The solution is heated and the iron is reduced with stannous chloride and then determined volumetrically with 0.05*N*-potassium permanganate solution using Zimmermann-Reinhardt's solution.[5]

Determination of Sulfur: Another portion of the sample solution is poured directly into the column of resin and washed with 150 cc. of water. The sulfate ion in the filtrate is precipitated with 10 per cent barium chloride solution and weighed as barium sulfate.

In order to check the results obtained, the sample was analysed by the usual method as follows:

After separating arsenic from iron with hydrogen sulfide, the element was determined volumetrically by conversion to silver arsenate and titration as in Volhard's method.[6]

From the filtrate of arseneous sulfide, iron was determined volumetrically with 0.05*N*-potassium permanganate solution as in the case of resin method. Sulfur was estimated gravimetrically as barium sulfate after separating it from iron with ammonia. Table 5 shows the data of these experiments. The results obtained are in fairly good agreement with each other.

Table 5

Data of Analysis of an Arsenopyrite

	Resin method, %	Common method, %
As	43.89	43.64
Fe	34.13	34.30
S	21.11	21.25
Total	99.13	99.19

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(4) The sample is from the Iname mine, Aichi Prefecture.

(5) C. Zimmermann, *Ber.*, **14**, 779 (1881); C. Reinhardt, *Z. anal. Chem.*, **36**, 794 (1897).

(6) W. Eschweiler and W. Röhrs, *Z. angew. Chem.*, **36**, 464 (1923).

On the Critical Concentration of *n*-Aliphatic Acid Salts and Similar Compounds

By Shunsuke SHISHIDO

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I. Introduction

It has been widely accepted that molecules of the soap dissolved in water are associated into grand molecules or micelles, owing to the cohesive interaction between their aliphatic long chain groups. However, properties of the micelle have little been studied theoretically, for examples, the form, dimension or electrolytic behaviour. Therefore, we can hardly explain the experimental facts and are troubled with complicated behaviours.

The aqueous solution of long chain fatty acid salts and the similar compounds (alkyl-

sulfonic, alkylsulfuric, alkylpyridium, alkyltrimethyl-ammonium salts, etc.) changes their properties complicately with increasing concentration and there appear some nick points on the curve of the properties against the concentration. The nick point which appears in the most dilute region among these nick points is understood tacitly as the formation of cmparatively small micelles from the monomolecularly dissolved systems. This concentration is called the critical concentration, which can be determined from this nick point.

In actual case, the critical concentration can be obtained from the observation of the nick point in the density, electric conductivity, viscosity, refractive index, optical absorption, and surface tension against the concentration of a salt. When these experimentally observed values are compared quantitatively with the theoretical ones and the reasonable coincidences are obtained, the circumstances of this micelle formation can be more discretely explained. Therefore, it is valuable to discuss the critical concentration theoretically.

II. Electric Energy of a Monomolecular and an Associated Ion of Soap

A soap molecule is considered to be consisted of three parts, R, $-COO^-$, and M^+. R is an aliphatic long chain group which is strongly hydrophobe, so that in aqueous solution they are apt to associate with each other. On the other hand, carboxyl radical, as well as, metal ion M^+ are hydrophile and they disperse in water. The net work of these associating and dispersing forces induces the formation of the stable micelle.

In water, the hydrophile property of carboxyl radical prevents itself from emboding in the alkyl group R, therefore it exists contacting directly with the water molecule (Fig. 1). Now the electrostatic energy of a spherical ion (radius ρ) charged with ε in water (dielectric constant $\mu = 80$ at 20°), is

$$\epsilon_0 = \frac{\varepsilon^2}{2\mu\rho}$$

If we assign the analogous energy to a carboxyl radical ion, the electrostatic energy of a fatty acid ion is expressed as follows:

$$\epsilon_1 = \epsilon_0 + \epsilon_1(A) \qquad (1)$$

where $\epsilon_1(A)$ is the extra electrostatic energy caused by the alkyl group (C_nH_{2n+1}) with low dielectric constant ($\mu_3 = 2.30$). First, we must estimate this extra energy. When the point charge exists on a point P, as shown in Fig. 1, the potential at a point excluding the point P is obtained by the expansion of the spherical harmonics (Appendix (I)). For example, the potential energy at Q in Fig. 1 is

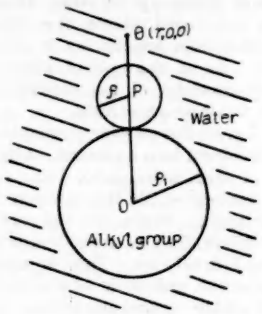

Fig. 1.

$$\Psi = \frac{\varepsilon}{\mu(\rho+\rho_1)}\left\{\frac{\rho+\rho_1}{r-(\rho+\rho_1)} + \sum_0^\infty \frac{\nu(\mu-\mu_3)}{\nu(\mu+\mu_3)+\mu}\,\frac{\rho_1^{2\nu+1}}{(\rho+\rho_1)^\nu r^{\nu+1}}\right\} \qquad (2)$$

The first term of this equation becomes infinite as $r \to (\rho+\rho_1)$, and if $r = \rho_1+2\rho$, it becomes $\varepsilon/\mu\rho$. Therefore we should consider that the first term is concerned of the self electrostatic energy ϵ_0 and the other terms represent extra $\epsilon_1(A)$ due to alkyl group. That is,

$$\epsilon_1(A) = \frac{\varepsilon^2}{2\mu(\rho+\rho_1)} \times \sum_0^\infty \frac{\nu(\mu-\mu_3)}{\nu(\mu+\mu_3)+\mu}\,\frac{\rho_1^{2\nu+1}}{(\rho+\rho_1)^{2\nu+1}} \qquad (3)$$

The estimated values are almost trivial (Table 1). The form of associated molecule is also considered to be spherical at the first approximation. The energy ϵ_n can be written,

$$\epsilon_n = n\epsilon_0 + \epsilon_n(A) \qquad (4)$$

where $\epsilon_n(A)$ is the extra energy relating to the centrally associated alkyl groups. Hereupon,

$$\epsilon_n(A) = \frac{1}{2} n\varepsilon\sum_2^n \Psi_n + n\epsilon_1(A, \rho_n) \qquad (5)$$

in which Ψ_n is the electrostatic potential at point P, due to the n-th $-COO^-$ radical and $\epsilon_1(A, \rho_n)$ is the value of Eq. (3) in which ρ_1 is replaced with ρ_n.

$\epsilon_n(A)$ approaches rapidly to the value of

$$\frac{n^2\varepsilon^2}{2\mu(\rho+\rho_n)} \qquad (6)$$

in the larger degree of association (Appendix (II)).

III. The Association of n-Fatty Acid Ions

The energy of a n-fatty acid ion in aqueous solution depends mainly on the interfacial energy between aliphatic group and water and on the electrostatic energy. Therefore fatty acid ions should be associated into a grand ion with appropriate degree of association owing to the counterbalancing action of the interfacial and electric energy in water. If we assume that the grand ion with n degrees of association is formed spherically, then the radius of this sphere, ρ_n, is

$$\frac{4\pi}{3}\rho_n^3 = nv, \quad \frac{4\pi}{3}\rho_1^3 = v \tag{7}$$

where v is the volume of an alkyl group. The interfacial energies are

$$\epsilon_1' = 4\pi\rho_1^2\sigma^* - \Delta \quad \text{for an ion,} \tag{8}$$

$$\epsilon_n' = 4\pi\rho_n^2\sigma^* - n\Delta \quad \text{for an associated ion,} \tag{9}$$

where σ^* is the microscopic interfacial free energy between alkyl group and water, and Δ is the contribution due to the connection part of alkyl group to $-COO^-$ radical.

The total energies are

$$\sum\epsilon_1 = \epsilon_0 + \epsilon_1(A) + 4\pi\rho_1^2\sigma^* - \Delta \quad \text{for an ion,} \tag{10}$$

$$\sum\epsilon_n = n\epsilon_0 + \epsilon_n(A) + 4\pi\rho_n^2\sigma^* - n\Delta \quad \text{for an associated,} \tag{11}$$

and the energy difference per molecule is

$$\begin{aligned}\Delta\epsilon &= \sum\epsilon_1 - (\sum\epsilon_n/n) \\ &= 4\pi\rho_1^2\sigma^* - 4\pi\rho_n^2\sigma^*/n + \epsilon_1(A) \\ &\quad - n\varepsilon^2/2\mu(\rho + \rho_n)\end{aligned} \tag{12}$$

The most probable degree of association is defined by

$$\partial(\Delta\epsilon)/\partial n = 0 \tag{13}$$

and is reduced to

$$\frac{4\pi}{3}\left(\frac{3}{4\pi}v\right)^{\frac{2}{3}}\sigma^* = \frac{\varepsilon^2}{2\mu}\frac{n}{\left(\frac{3v}{4\pi}\right)^{\frac{1}{3}} + \frac{\rho}{n^{\frac{1}{3}}}} \times \left\{1 - \frac{1}{3}\frac{\left(\frac{3}{4\pi}v\right)^{\frac{1}{3}}}{\left(\frac{3v}{4\pi}\right)^{\frac{1}{3}} + \frac{\rho}{n^{\frac{1}{3}}}}\right\} \tag{14}$$

From this condition, $n(\rho_n)$ is determined for the appropriate σ^*, and $\Delta\epsilon$ can be calculated with Eq. (12).

There are many molecules with various dergees of association in an aqueous solution of fatty acid salt, and the equilibrium schemes are

$$A_n \rightleftarrows A_{n-1} + A_1, \quad A_{n-1} \rightleftarrows A_{n-2} + A_1, \text{ etc.,}$$

where A_n is the molecule with n-degree of association. If the partition functions of these molecules write Z_n, the equilibrium conditions are given as follows according to the statistical thermodynamic way to the dilute solution,

$$\frac{Z_{n-1}Z_1}{Z_n} = \frac{N_{n-1}N_1}{N_0N_n}, \quad \frac{Z_{n-2}Z_1}{Z_{n-1}} = \frac{N_{n-2}N_1}{N_0N_{n-1}}$$

$$\therefore \quad \frac{Z_1^n}{Z_n} = \frac{N_1^n}{N_0^{n-1}N_n} \tag{15}$$

in which N_0 is the number of the water molecules in the system and N_n is the number of the associated molecule A_n.

When the concentration C is expressed in mol/l., N_n is C_nN and N_0 is $1000\times N/18$, in which N is the Avogadro's number, Eq. (15) is reduced to

$$\frac{C_n}{C_1} = \left(\frac{C_1}{\frac{1000}{18}\left(\frac{Z_1^n}{Z_n}\right)^{\frac{1}{n-1}}}\right)^{n-1} = \left(\frac{C_1}{C_0}\right)^{n-1},$$

where $$C_0 = \frac{1000}{18}\left(\frac{Z_1^n}{Z_n}\right)^{\frac{1}{n-1}}. \tag{16}$$

We define the critical concentration C_c for the most probable degree of association as the apparent concentration at $C_n = C_1$ ($C_1 = C_0$),

$$C_c = (n+1)C_0 = (n+1)\frac{1000}{18}\left(\frac{Z_1^n}{Z_n}\right)^{\frac{1}{n-1}} \tag{17}$$

Then, the behaviour of C_n/C_1 versus $C(= C_1 + nC_n)$ is very characteristic. In the case of $C_1 < C_0$ ($C < C_c$), C_n/C_1 is far smaller than unity, but in the case of $C_1 > C_0$ ($C > C_c$), C_n/C_1 is far larger than unity, since n is usually far larger than unity. The property which depended mainly on the associated molecule is not distinguishable until C reaches to C_c but predominant beyond C_c. It is the nick point on the curve of property against concentration as shown in Fig. 3.

Rewriting the partition function Z as below

$$Z = Z_0 e^{-\sum \varepsilon/kT} \quad \text{etc.,} \qquad (18)$$

$\exp(-\sum \in/kT)$ is the part owing to the energy of electrostatic and interfacial free energies, and Z_0 is the other part which is not mainly depended on the degree of association. C_c is expressed as

$$C_c = \frac{1000}{18}(n+1)e^{-\frac{n}{n-1}\frac{\Delta\epsilon}{kT}} \qquad (19)$$

where $\Delta\in$ is the value for the most probable degree of association.

IV. Calculated and Observed Values

Critical Concentration.—The values dotted in Fig. 4 are the experimental results which have been proceeded at various temperatures (18°—60°)(1). Fortunately, the critical con-

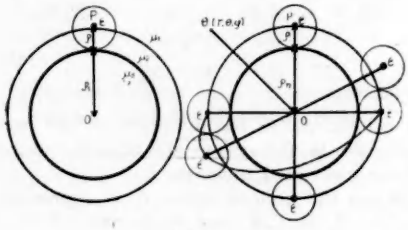

Fig. 2.

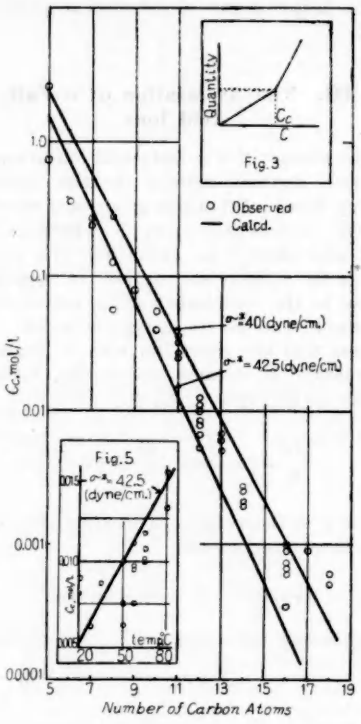

Fig. 4.

Table 1

No. of C atoms in alkyl radical R		5	6	8	10	12	14	16	18
Density of hydrocarbon HR at 20°C.		0.621	0.655	0.694	0.723	0.752	0.765	0.775	0.777
$\rho_1 \times 10^8$, cm.		3.58	3.73	4.02	4.26	4.47	4.67	4.86	5.05
$\epsilon_1(A) \times 10^{14}$, erg		0.7		0.9		1.0			1.1
$4\pi\sigma^*\rho_1^2 \times 10^{14}$, erg	σ^*=40, dyne/cm.	64.3	69.8	81.0	91.2	101	110	119	128
	=42.5	67.3	74.2	86.1	97.0	107	117	126	136
Degree of Association n	=40	9.0	10	12.5	15	17	19	21.5	24
	=42.5	9.5	11	13	15.5	18	20.5	23	25.5
$\rho_n \times 10^8$, cm.	=40	7.5	8.0	9.3	10.3	11.4	12.5	13.5	14.5
	=42.5	7.7	8.2	9.5	10.6	11.6	12.7	13.8	14.8
$\frac{4\pi\sigma^*\rho_n^2}{n} \times 10^{14}$, erg	=40	30.9	32.2	34.9	37.2	39.5	41.1	42.5	44.5
	=42.5	31.4	33.7	36.3	38.9	40.9	42.8	44.5	46.4
$\frac{n\varepsilon^2}{2\mu(\rho+\rho_n)} \times 10^{14}$, erg	=40	14.1	14.7	16.3	17.3	18.3	19.3	20.2	21.0
	=42.5	14.7	15.4	16.9	18.0	19.0	20.1	21.0	22.0
$\Delta\in \times 10^{14}$, erg	=40	20.0	23.5	30.5	37.5	44.0	50.5	57.0	63.5
	=42.5	22.0	26.0	33.5	41.0	48.0	55.0	61.5	69.0
Crit. conc. C_c, equiv./l.	=40	2.5	1.0	0.25	6×10^{-2}	1.3×10^{-2}	3×10^{-3}	7×10^{-4}	1.7×10^{-4}
	=42.5	1.5	0.9	0.10	2.5×10^{-2}	5×10^{-3}	1.3×10^{-3}	2.0×10^{-4}	5×10^{-5}

(1) K. Hess, *Kolloid Z.*, **88**, 40(1939); *J. Am. Chem. Soc.*, **61**, 322, 539, 544, 549(1939); Jander and Weitendorf, *Z. anorg. Chem.*, **41**, 197(1934); Bury and Parry, *J. Chem. Soc.*, 629(1935); Howell, *Proc. Roy. Soc.*, **A 115**, 386(1936); Lottermoser, *Kolloid Z.*, **63**, 175(1935); Hartley, *Trans. Faraday Soc.*, **34**, 799, 1298, 2348(1938); Ekwell, *Z. physik. Chem.*, **A 161**, 195(1932); Ulmann, *Z. physik. Chem.*, **A 182**, 18(1938).

Table 2

Temp. °C	Density of HR	μ	C_c, equiv./l. calc.
20	0.752	80.0	0.005
40	0.738	73.0	0.008
60	0.722	66.8	0.011
80	0.708	61.8	0.015

(σ^*=42.5 dyne/cm.)

centrations are not so greatly changed in these temperature intervals, that we can plot these observed values without serious consideration about temperature at which the experiments were proceeded.

In order to calculate the critical concentration with Eq. (17), we are to assign the appropriate value for the volume of an alkyl-group. This is done by the calculation of molecular volume of the corresponding n-hydrocarbon at 20°. In Table 1, the calculated values are listed and the critical concentration at 20° for σ^*=40 dyne/cm. and 42.5 dyne/cm. are shown by straight lines in Fig. 4.

Dependence on Temperature.—Since observed interfacial tension between water and hydrocarbon scarcely varies with temperature, we assume that the microscopic interfacial tension is also constant with temperature. Now dependence on temperature of critical concentration can be calculated easily, on which dielectric constant of water and temperature are mainly effecting. Observed and calculated values for dodecyl $C_{12}H_{26}$-group derivatives are shown in Table 2 and Fig. 5.

Generally, the coincidences between observed and calculated values are satisfactory. The slope of the curve for calculated values is steeper than the observed. This would be caused from the fact that the observations for higher homologues ($C_{15}H_{31}-$, $C_{16}H_{33}-$, $C_{17}H_{35}-$, $C_{18}H_{38}-$, etc.) were done at higher temperature (~60°) than the culculation (20°), so that the observed critical concentrations are larger. It can be very easily accepted also that the microscopic interfacial tension between n-octane and water is as large as 42 dyne/cm., because the interfacial tension between n-octane and water is as large as 50 dyne/cm. at 20°.

I think that the procedure mentioned above is valuable for the estimation of microscopic interfacial free energy between water and aliphatic groups.

Appendix

(I) There is an electric system as shown in Fig. 2, in which the point charge exists at a outer point P. The potential at the point (r,θ,φ) excluding P, is the solution of Laplacian equation $\nabla^2\phi = 0$. Namely,

$$\phi = \sum_\nu \left(A_\nu r^\nu + \frac{B_\nu}{r^{\nu+1}} \right) S_\nu \qquad (20)$$

where A_ν and B_ν are coefficients and S_ν is spherical harmonics.

When we divide the space into three parts; outer ($r \geq \rho + \rho_1$), mediate ($\rho + \rho_1 \geq r \geq \rho$) and inner ($r \leq \rho_1$), the potential in these regions are respectively

$$\left.\begin{aligned} \phi_1 &= \sum_\nu \frac{{}_1B_\nu}{r^{\nu+1}} P_\nu(\cos\theta) \\ \phi_2 &= \sum_\nu \left({}_2A_\nu r^\nu + \frac{{}_2B_\nu}{r^{\nu+1}} \right) P_\nu(\cos\theta) \\ \phi_3 &= \sum_\nu ({}_3A_\nu r^\nu P_\nu(\cos\theta) \end{aligned}\right\} \qquad (21)$$

where S_ν is replaced by P_ν, because the potential is completely symmetrical about Z axis. Of course, the electric charge should be considered as distributed on the sphere surface with radius $\rho + \rho_1$, which is expanded with spherical harmonics. Therefore, the surface charge at $(\rho + \rho_1, \theta, \varphi)$ is expressed as

$$\sigma = \sum_\nu \frac{(2\nu+1)\varepsilon}{4\pi(\rho+\rho_1)} P_\nu(\cos\theta) \qquad (22)$$

The boundary conditions are

$$\left.\begin{aligned} \phi_1 = \phi_2,\ -\mu_1 \frac{\partial\phi_1}{\partial r} + \mu_2 \frac{\partial\phi_2}{\partial r} &= -4\pi\sigma \\ \text{at } r &= \rho + \rho_1 \\ \phi_2 = \phi_3,\ -\mu_2 \frac{\partial\phi_2}{\partial r} + \mu_3 \frac{\partial\phi_3}{\partial r} &= 0 \\ \text{at } r &= \rho_1 \end{aligned}\right\} \qquad (23)$$

where $\mu_1 = \mu_2 (= \mu)$ and μ_3 are dielectric constants. From these boundary conditions and orthogonality of P_ν, the following equations are obtained:

$$\left.\begin{aligned} {}_1A_\nu(\rho+\rho_1)^\nu + \frac{{}_2B_\nu}{(\rho+\rho_1)^{\nu+1}} &= \frac{{}_2B_\nu}{(\rho+\rho_1)^{\nu+1}} \\ \frac{(\nu+1){}_1B_\nu}{(\rho+\rho_1)^{\nu+2}} + \nu_2A_\nu(\rho+\rho_1)^{\nu-1} & \\ -\frac{(\nu+1){}_2B_\nu}{(\rho+\rho_1)^{\nu+2}} &= -\frac{(2\nu+1)\varepsilon}{\mu(\rho_1+\rho)^2} \\ {}_3A_\nu\rho_1^\nu = {}_2A_\nu\rho_1^\nu + \frac{{}_2B_\nu}{\rho_1^{\nu+1}} & \\ \mu_3\,{}_3A_\nu - \mu\left\{ {}_2A_\nu - \frac{(\nu+1){}_2B_\nu}{\rho^{\nu+2}} \right\} &= 0 \end{aligned}\right\} \qquad (24)$$

Solving these simultaneous equations, we get

the values for coefficients A and B. Potential at point Q ($r \geq \rho + \rho_1$) is

$$\phi_1^* = \frac{\varepsilon}{\mu(\rho+\rho_1)} \times \left\{ \frac{\rho+\rho_1}{r\sqrt{1-\frac{2(\rho+\rho_1)}{r}\cos\theta+\left(\frac{\rho+\rho_1}{r}\right)^2}} + \sum_0^\infty \frac{\nu(\mu-\mu_3)}{\nu(\mu+\mu_3)+\mu} \frac{\rho_1^{2\nu+1} P_\nu(\cos\theta)}{(\rho+\rho_1)^{\nu\nu+1}} \right\} \quad (25)$$

Table 3

Charge	Figure	Point charge system: Energy (P)	Surface charge system: Energy (S)	Ratio (S/P)
2ε		$\frac{1}{2}\frac{\varepsilon^2}{r}$	$2\frac{\varepsilon^2}{r}$	4.00
3ε		$\sqrt{3}\frac{\varepsilon^2}{r}$	$4.5\frac{\varepsilon^2}{r}$	2.60
4ε		$\frac{3\sqrt{3}}{\sqrt{2}}\frac{\varepsilon^2}{r}$	$8\frac{\varepsilon^2}{r}$	2.18
6ε		$(6\sqrt{2}+1.5)\frac{\varepsilon^2}{r}$	$18\frac{\varepsilon^2}{r}$	1.80
8ε		$(6\sqrt{3}+3\sqrt{2}+2)\times\frac{\varepsilon^2}{r}$	$32\frac{\varepsilon^2}{r}$	1.65
12ε		$(6\sqrt{2}+8\sqrt{3}+27)\frac{\varepsilon^2}{r}$	$72\frac{\varepsilon^2}{r}$	1.46

From this equation, (2) can be derived for $\theta = 0$, $\cos\theta = 1$.

(II) We may compare the electrostatic energy of the point charge system with that of the spherical surface charge. The ratio approaches to unity when the number of charges becomes larger, as shown in Table 3. Now let us estimate the electrostatic energy of the system shown in Fig. 2, which is the degree of association 6, $\rho_6 = 6.03$ Å. (for oenanthylic acid ions), and $\rho = 1.80$ Å.

The estimation is easy, because $P_\nu(\cos\theta)$ in Eq. (25) are simple for $\theta = 0$, $\pi/2$ and π. The potential energy at P due to the other five charges is

$$\Psi = 4\phi_6(\cos\theta = 0) + \phi_6(\cos\theta = -1)$$

in which ϕ_6 is the value for $r = \rho + \rho_6$ and $\rho_1 \to \rho_6$ in Eq. (25) and therefore the electrostatic energy is

$$\frac{1}{2}6\varepsilon\Psi + 6\epsilon_i(A_1\rho_6) = 13.1\frac{\varepsilon^2}{\mu(\rho+\rho_6)}$$

for $\mu = 80$ and $\mu_3 = 2.3$.

Comparing it with the case of $\mu_3 = \mu = 1$ (Table 3), this value is more close to the surface charge 6ε on the sphere with radius $\rho + \rho_6$, *i. e.*, $18.0\,\varepsilon^2/\mu(\rho+\rho_6)$

Therefore, we may safely replace the point charge system with the spherical surface charge for much larger degree of association.

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Adsorption of Carbon Dioxide on Metal Catalysts

By Takao KWAN and Yuzabro FUJITA

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One of the present authors recently investigated the adsorption of carbon monoxide on platinum catalyst[1] with special reference to its state on platinum, and concluded that it was dissociated into statistically independent atoms. Developing the method further, carbon dioxide adsorption was now investigated on reduced nickel, cobalt and iron respectively.

Adsorption isotherm of carbon dioxide is derived by introducing a set of functions p, q and θ due to Horiuti,[2] respectively for the undissociative adsorption $CO_2 \rightleftarrows CO_2(a)$, for the

(1) Kwan, *J. Res. Inst. Catalysis*, Vol. 1, No. 2, 110 (1949).

(2) Horiuti, *J. Res. Inst. Catalysis*, Vol. 1, No. 1, 8 (1948).

partially dissociative one, $CO_2 \rightleftarrows CO(a) + O(a)$, and for the completely dissociative one into three statistically independent atoms, $CO_2 \rightleftarrows C(a) + O(a) + O(a)$, as follows;

$$\frac{\theta}{1-\theta} = \frac{q^{CO_2(a)}}{p^{CO_2(a)}} \tag{1.1}$$

$$\frac{\theta}{1-2\theta} = \frac{q^{CO(a)}}{p^{CO(a)}} = \frac{q^{O(a)}}{p^{O(a)}} \quad (3) \tag{1.2}$$

$$\frac{\theta}{1-3\theta} = \frac{q^{C(a)}}{p^{C(a)}} = \frac{q^{O(a)}}{p^{O(a)}} = \frac{q^{O(a)}}{p^{O(a)}} \quad (3) \tag{1.3}$$

where θ is the covered fraction of the surface and $q^{CO_2(a)}$, $q^{CO(a)}$, $q^{C(a)}$ and $q^{O(a)}$ are the functions particular to the adsorbed states $CO_2(a)$, CO(a), C(a) and O(a) expressed as,

$$q^{CO_2(a)} = \prod^{i} (1 - e^{-\frac{h\nu_i}{kT}})^{-1} e^{-\frac{\varepsilon_0 + \frac{1}{2}h\Sigma\nu_i}{kT}}, \text{etc.} \tag{2.q}$$

and $p^{CO_2(a)}$, $p^{CO(a)}$, $p^{C(a)}$ and $p^{O(a)}$ are related with the chemical petentials $\mu^{CO_2(a)}$, $\mu^{CO(a)}$, $\mu^{C(a)}$ and $\mu^{O(a)}$ of CO_2(a), CO(a), C(a) and O(a) as,

$$\mu^{CO_2(a)} = -RT \log p^{CO_2(a)}, \text{ etc.} \tag{2.p(a)}$$

and p^{CO_2} with the chemical potential of gaseous carbon dioxide μ^{CO_2} and hence with the ordinary partition function Q and its concentration N as,

$$\mu^{CO_2} = -RT \log p^{CO_2} = -RT \log Q/N \tag{2.p}$$

At adsorption equilibrium we have

$$\mu^{CO_2} = \mu^{CO_2(a)} \tag{3.1}$$

$$\mu^{CO_2} = \mu^{CO(a)} + \mu^{O(a)} \tag{3.2}$$

$$\mu^{CO_2} = \mu^{C(a)} + \mu^{O(a)} + \mu^{O(a)} \tag{3.3}$$

respectively for the case when CO_2 molecule is undissociated, partially dissociated or completely dissociated at the adsorbed state. From Eqs. (1), (2) and (3) we have

$$\frac{\theta}{1-\theta} = \frac{N q^{CO_2(a)}}{Q} \tag{4.1}$$

$$\left(\frac{\theta}{1-2\theta}\right)^2 = \frac{N q^{CO(a)} q^{O(a)}}{Q} \tag{4.2}$$

$$\left(\frac{\theta}{1-3\theta}\right)^3 = \frac{N q^{C(a)} q^{O(a)} q^{O(a)}}{Q} \tag{4.3}$$

Eqs. (4.1), (4.2) and (4.3) are expressed further in terms of the measurable quantities such as the equilibrium pressure P and the differential heat of adsorption per mole $\Delta\varepsilon$ neglecting the contribution from the higher vibrational levels of gaseous carbon dioxide molecules and for the case $\theta \ll 1$ as[4]

$$\theta = \frac{q^{CO_2(a)} e^{T\frac{\partial \log q^{CO_2(a)}}{\partial T}}}{Q_0} P e^{\frac{\Delta\varepsilon}{RT}} \tag{5.1}$$

$$\theta^2 = \frac{q^{CO(a)} q^{O(a)} e^{T\frac{\partial \log q^{CO(a)} q^{O(a)}}{\partial T}}}{Q_0} P e^{\frac{\Delta\varepsilon}{RT}} \tag{5.2}$$

$$\theta^3 = \frac{q^{C(a)} q^{O(a)} q^{O(a)} e^{T\frac{\partial \log q^{C(a)} q^{O(a)} q^{O(a)}}{\partial T}}}{Q_0} P e^{\frac{\Delta\varepsilon}{RT}} \tag{5.3}$$

where

$$Q_0 = kT \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 IkT}{sh^2} e^{\frac{7}{2}}$$

The investigation of the factors

$$q^{CO_2(a)} e^{T\frac{\partial \log q^{CO_2(a)}}{\partial T}}, \text{ etc.}$$

in the above equations shows that every one of them is generally greater than 1 and approaches 1 as $h\nu_i \gg kT$. Assuming that the latter condition is fulfilled, we have

$$\left.\begin{matrix}\theta \\ \theta^2 \\ \theta^3\end{matrix}\right\} = P e^{\frac{\Delta\varepsilon}{RT}} / Q_0 \qquad \begin{matrix}(6.1) \\ (6.2) \\ (6.3)\end{matrix}$$

The above equations give relations between θ and P respectively appropriate to the three different adsorbed states affording a method of experimental determination of them.

Materials

Reduced Nickel.—1 g. of nickel oxide obtained by igniting the basic carbonate at 500° was thoroughly reduced at 350° similarly as described in the previous paper[4] under several cm. Hg hydrogen for several days keeping the catalyst from volatile matter which might be evolved from stop-cock grease by means of liquid air trap attached directly to the catalyst vessel. The reduced nickel powder thus prepared was then subjected to the adsorption experiment of carbon dioxide and thereafter to the determination of the surface area by B. E. T. method using nitrogen at liquid oxygen temperature and the surface area was found to be 20 m^2.

(3) The s must be equal because of the stoichiometrical relation for CO(a) and O(a) or for C(a), O(a) and another O(a).

(4) *Cf.* Kwan, *J. Res. Inst. Catalysis*, Vol. 1, No. 2, 81 (1949).

Reduced Cobalt.—Reduced cobalt prepared by reducing 0.5 g. of cobalt oxide at 450° and once used for hydrogen adsorption was used again. The B. E. T. area of the catalyst was 7 m^2.

Reduced Iron.—Reduced iron prepared by reducing 2 g. of magnetite at 500° and once used for hydrogen adsorption and then for carbon monoxide adsorption as well was used again. The B. E. T. area of the catalyst was 4.2 m^2.

Carbon Dioxide.—Carbon dioxide was prepared by igniting sodium bicarbonte in an evacuated tube and traces of air and water vapors were removed by fractionation with liquid air.

Experimental Procedure

The apparatus and the general procedure for the measurement of adsorption equilibrium are identical with those of the previous paper.[4] After any of the reduced metal catalysts has been prepared, U-trap is surrounded by copper gauge filled with copper powder whose bottom being slightly dipped into liquid air, then the temperature of U-trap can be kept at about −60° avoiding the condensation of carbon dioxide inside the U-tube on one hand and freezing out traces of volatile matter from stop-cock grease on the other.

The catalyst is then evacuated by means of mercury diffusion pump for one hour at 350°, one hour at 400° and one hour at 500° for nickel, cobalt and iron respectively. The known quantity of carbon dioxide is then admitted into the reaction vessel, which is maintained at a desired temperature by the electric furnace through the U-trap and the decrease in pressure is followed by McLeod gauge. After letting it stand for about 20 hours the equilibrium pressure is determined both from adsorption and desorption side by lowering or raising the temperature of the furnace.

Adsorbed quantity x is given by

$$x = P_0V_0/RT - \alpha P,$$

where P_0V_0/RT is the quantity of carbon dioxide initially taken and P the equilibrium pressure. α is the constant depending on the temperature of the reaction vessel and is determined preliminarily keeping any part of the apparatus precisely the same but without a catalyst.

Additional portion of carbon dioxide is then succesively admitted and the corresponding equilibrium pressure is similarly determined in respective cases.

Results

Nickel.—The rate of adsorption and of desorption as well were found appreciably quick as was in the case of hydrogen adsoption on this catalyst, suggesting that adsorption equilibrium was instantaneously attained. Any of equilibrium pressures was however determined, after being left standing for about 20 hours, by approaching it both from adsorption and desorption side. Adsorption isotherms thus determined at 150° and 200° and at pressure ranging from 10^{-4} to 10^{-1} mm. Hg are shown by the plot of logarithm of the adsorbed quantities against logarithm of the equilibrium pressure in Fig. 1. As shown in

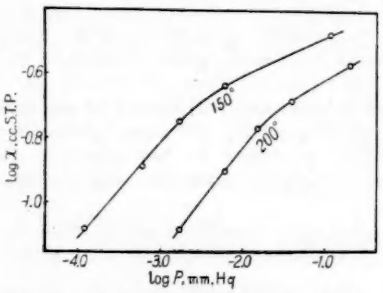

Fig. 1.—Adsorption isotherms of CO_2 on reduced nickel.

Fig. 1 the adsorbed quantity was found to be proportional to 1/3 power of the equilibrium pressure at the lower degree of adsorption, decreasing rapidly with increasing adsorption. It is apparent from the result that carbon dioxide adsorption takes place according to Eq. (6.3) viz. with completely dissociative adsorption at least in the lower pressure region.

Differential heat of adsorption $\Delta\varepsilon$ calculated from the isotherms according to the usual expression $\Delta\varepsilon = RT^2(\partial \log P/\partial T)_x$ was almost constant at 22 kcal./mole over the range of the smaller adsorption.

Using the heat of adsorption derived, the covered fraction θ_{calc} was now calculated at 200° according to Eqs. (6.1), (6.2) or (6.3) and compared in Fig. 2 with θ_{obs} derived from the adsorbed quantity and the B. E. T. area of the adsorbent assuming that 10^{15} nickel atoms per square centimeter were available and each atom was equally capable of adsorbing CO_2(a), CO(a), C(a) or O(a)[5].

It is obvious that θ_{obs} agrees fairly well with θ_{calc} derived from Eq. (6.3) and not with that from Eq. (6.1) or (6.2), hence showing that carbon dioxide molecule dissociates into three statistically independent atoms. Somewhat small value of θ_{calc} may be probably attributed to the simplification that $h\nu_i \gg kT$ in q's,

(5) In the case of undissociative or partially dissociative adsorption, θ_{obs} may be more or less different according as whether CO_2 (a) or CO (a) occupies how many atoms of nickel. But this would be rather ignored as far as three adsorbed states, mentioned above, concern where θ_{calc}s in interest are much more differed with each other.

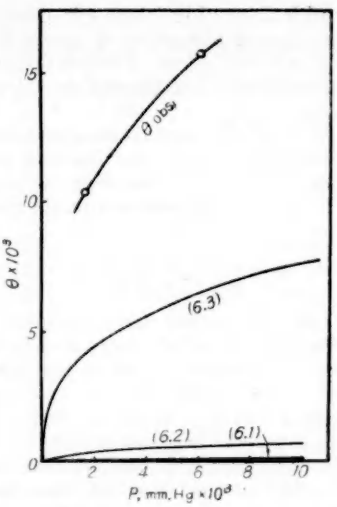

Fig. 2.—The relation between θ and P on reduced nickel, $T=200°C$.

although we have no available data with respect to ν_is of C(a) or O(a).

In the case of the adsorbed hydrogen atom H(a) on reduced nickel, Horiuti and coworkers[6] obtained three vibrational frequencies by calculation as

$$417\ \text{cm.}^{-1} \quad 479\ \text{cm.}^{-1} \quad 1900\ \text{cm.}^{-1}$$

taking into consideration the potential of the surrounding nickel atoms upon the adsorbed hydrogen atom for the (110) plane.

On the basis of these values the calculation of the factor $q^{H(a)}e^{T\frac{\partial \log q^{H(a)}}{\partial T}}$ was carried out, affording 7, 5 and 2 at 300°, 200° and 20° respectively. The experimental facts on reduced nickel or cobalt[3] however revealed, as reported previously, that the above factor was approximately 1, giving no temperature effect below 300°. It seems likely that the assumption $h\nu_i \gg kT$ in q's hold enough as far as the hydrogen adsorption on these catalysts concerns.

Reduced Cobalt.—Adsorption isotherms of carbon dioxide on reduced cobalt were determined similarly as those of reduced nickel at 0° and 40° and below 0.1 mm. Hg as shown in Fig. 3. The isotherms appear to obey nearly Freundlich's type in this case, probably missing such a lower degree of adsorption as proportional to 1/3 power of the equilibrium pressure.

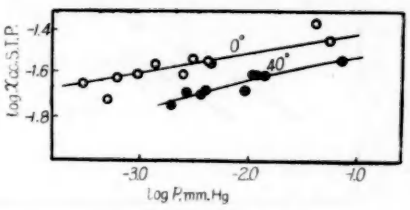

Fig. 3.—Adsorption isotherms of carbon dioxide on reduced cobalt.

Differential heat of adsorption calculated therefrom was found to be 14 kcal./mole. Using the heat of adsorption derived, θ_{calcs} were calculated at 0° similarly as in the case of nickel and were compared in Fig. 4 with θ_{obs} showing the satisfactory agreement of the latter with θ_{calc} derived from Eq. (6.3) at a very low degree of adsorption and θ_{obs} rapidly flattened with increasing adsorption.

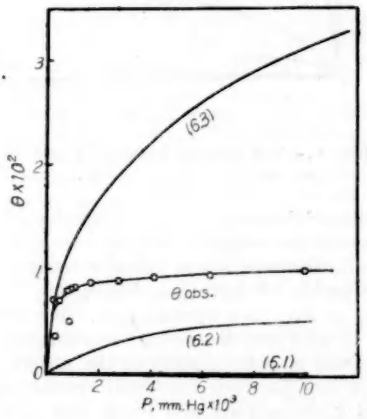

Fig. 4.—The relation between θ and P on reduced cobalt. $T=0°C$.

Reduced Iron.—The adsorption isotherms on reduced iron determined at 0° and 25° similarly as in the case of nickel or cobalt are shown in Fig. 5. Differential heat of adsorption calculated therefrom was found to be 15.5 kcal./mole at the lower degree of adsorption. The plot of the covered fraction θ_{obs} against the equilibrium pressure P in the present case lies without agreeing with any θ_{calc} given by Eqs. (6.1), (6.2), (6.3) as shown in Fig. 6, being more or less differed from the results given by the two catalysts cited above.

(6) Horiuti, Okamoto and Hirota, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **29**, 223(1936).

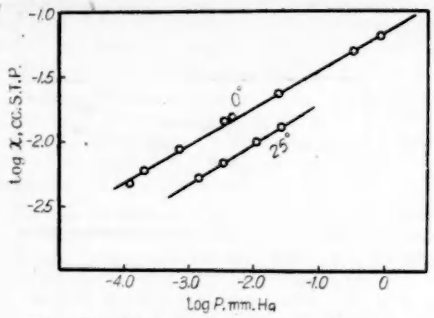

Fig. 5.—Adsorption isotherms of carbon dioxide on reduced iron.

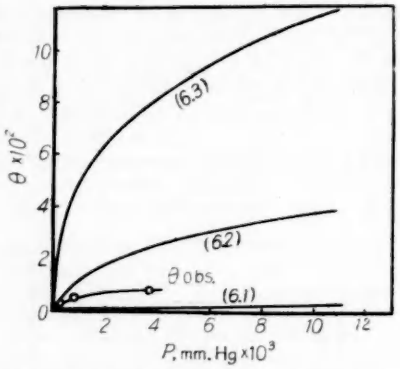

Fig. 6.—The relatien between θ and P on reduced iron. T=0°C.

It should be however remembered that the surface of the reduced iron is not homogeneous on the basis of the statistical mechanical investigation of hydrogen adsorption,[7] exposing at least two crystal planes. We hereby have to take into consideration quantitatively the extent of heterogeneity of the surface.

It is now assumed that two crystal planes 1 and 2 are exposed and every iron atom at the surface behaves physically identical even in the case of carbon dioxide adsorption, namely, the corresponding heats of adsorption of carbon dioxide $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ appear identically with those of hydrogen adsorption. The observed heat of adsorption of carbon dioxide $\Delta\varepsilon$ at a very low degree of adsorption would hence reveal $\Delta\varepsilon_1$ of the plane 1 provided that $\Delta\varepsilon_1 \gg \Delta\varepsilon_2$.

The ratio of $\theta_{obs.}$ to $\theta_{calc.}$ calculated statistical mechanically using the observed heat of adsorption $\Delta\varepsilon$ means the fraction of that "active" plane 1 as described in the previous paper, *i. e.*

$$\frac{\theta_{obs.}}{\theta_{calc.}} = \frac{N_1}{N_1+N_2}$$

where N_1 and N_2 are the numbers of iron atom respectively belong to the plane 1 and 2. N_1/N_1+N_2 is about 1/100 according to the previous investigation of this catalyst. Hence multiplying 100 to $\theta_{obs}/\theta_{calc}$ we find a better agreement between θ_{obs} and θ_{calc} derived from Eq. (6.3) with regard to the order of magnitude, leading to the same conclusion on the adsorbed state of carbon dioxide as in the case of nickel or cobalt.

Summary

Differential heat of adsorption of carbon dioxide on reduced nickel, cobalt or iron catalyst was determined by the indirect method at the lower degree of adsorption with particular precaution for securing thermodynamical equilibrium, being found at 22, 14 and 15,5 kcal./mole respectively. Using the heat of adsorption derived adsorption isotherms were investigated statistical mechanically with reference to the adsorbed state of carbon dioxide molecule, leading to the conclusion that the molecule dissociates into three statistically independent atoms in any case of the catalysts.

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(7) Kwan, *J. Res. Inst. Catalysis*, Vol. 1, No. 2, 100 (1949).

Synthesis of 2-Arylimino-3-aryl-4-keto-tetrahydrothiazoles by Condensing Di-Arylthioureas with Monochloroacetic Acid

By Prithwi Nath Bhargava

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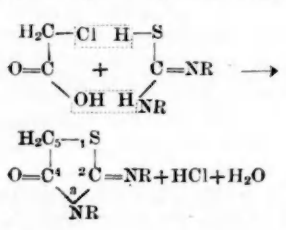
A number of sulfathiazoles have been known for their therapeutic properties and have been universally used as drugs. Amidothiazoles and their isomers were reported by Jacobson[1] and Jacobson and Ney.[2] Nitroso-compounds of thiazoles were synthesised previously by Hantzsch[3] and Hantzsch *et al.*[4] Goldberg and Kelley[5] synthesised 2-ω-aminoalkyl- and 2-ω-sulfanilamidoalkyl derivatives of thiazoles. Gregory and Wiggins[6] studied 2:4-dimethyl-thiazole derivatives and 2:4:5-trimethyl thiazole. Recently Alexander R. Surrey has prepared 3-alkyl (and aralkyl) -2-aryl-4-thiazolidones[7] and 3-alkylaminoalkyl-2-aryl-4-thiazolidones.[8]

The author has carried out the condensations of monochloroacetic acid with diphenylthiourea, di-*o*-tolylthiourea, di-*p*-tolylthiourea, di-α-naphthylthiourea, di-β-naphthylthiourea, di-*p*-anisylthiourea, and di-*p*-phenetylthiourea. The general method of preparation is analogous to the formation of 2-imino-4-keto-tetrahydrothiazole[9],[10] by condensing thiourea with monochloroacetic acid and subsequently dehydrating by heating with glacial acetic acid.



The synthesis has been accomplished on standard lines, thereby showing the constitution of the compounds. All these condensation products are solids of high melting points.

The formation of semicarbazones of the respective compounds gives evidence regarding the presence of a keto-group.

Experimental

2-Phenylimino-3-phenyl-4-keto-tetrahydrothiazole.—To a mixture of thiocarbanilide (22.8 g.), monochloroacetic acid (12.0 g.) and finely powdered anhydrous sodium acetate (12.3 g.) in a dry flask was added 50 cc. of absolute alcohol and the above boiled on a water-bath for 2 hours. Towards the end of the condensation, some of the product separated in leaflets. The major portion of the alcohol was distilled off and the contents of the flask were poured out into a porcelain dish to crystallise. The crystals were washed with cold water to remove excess of monochloroacetic acid. It was purified by recrystallising three times from hot absolute alcohol. Colorless laminae (23.76 g.), m. p. 176° (Found: N, 10.45. Calcd. for $C_{15}H_{12}N_2OS$: N, 10.44%).

Semicarbazone.—The above 2-phenylimino-3-phenyl-4-keto-tetrahydrothiazole (250 mg.) was dissolved in 95% alcohol (20 cc.) and to this semicarbazide hydrochloride (300 mg.) and anhydrous sodium acetate (500 mg.) were added. The whole mixture was refluxed for 15 minutes and poured into water. The crystals were collected and recrystallised from absolute alcohol in needles, m. p. 194° (Found : N, 21.58. Calcd. for $C_{16}H_{15}N_5OS$: N, 21.53%).

2-*o*-Tolylimino-3-*o*-tolyl-4-keto-tetrahydrothiazole.—A suspension of di-*o*-tolylthiourea (12.4 g.) in absolute alcohol (50 cc.) was heated under reflux with monochloroacetic acid (6.0 g.) and anhydrous sodium acetate (6.0 g.) for 2 hours. The condensation was effected, and the product was isolated as described above. The residue on crystallisation from absolute alcohol and drying in vacuum at 110° over phosphorus pentoxide yielded white needles (12.18 g.), m. p. 154–155° (Found : N, 9.44. Calcd. for $C_{17}H_{16}N_2OS$: N, 9.46%).

Semicarbazone.—2-*o*-Tolylimino-3-*o*-tolyl-4-keto-tetrahydrothiazole (260 mg.) was dissolved in 95% alcohol (20 cc.) and refluxed with semicarbazide hydrochloride (300 mg.) and anhydrous sodium acetate (300 mg.) for 20 minutes. On pouring the mixture into water (80 cc.) a precipitate was obtained, which was crystallised from absolute alcohol in leaflets, m. p. 182° (Found: N, 19.85; calcd. for $C_{18}H_{19}N_5OS$: N, 19.83%).

2-*p*-Tolylimino-3-*p*-tolyl-4-keto-tetrahydro-

(1) Jacobson, *Ber.*, **19**, 1067 (1886).
(2) Jacobson and Ney, *ibid.*, **22**, 904 (1889).
(3) Hantzsch, *Ann.*, **262**, 250 (1889).
(4) Hantzsch *et al.*, *ibid.*, **265**, 108 (1889).
(5) Goldberg and Kelley, *J. Chem. Soc.*, **1947**, 1572.
(6) Gregory and Wiggins, *ibid.*, **1947**, 1400.
(7) Alexander R. Surrey, *J. Am. Chem. Soc.*, **70**, 4262. (1948).
(8) Alexander R. Surrey, *ibid.*, **71**, 3354 (1949).
(9) P. N. Bhargava, *Proc. Ind. Sci. Cong. Chem. Sec. Abst.*, **1949**, 78.
(10) R. D. Desai, R. F. Hunter and L. G. Koppar, *Rec. trav. chim.*, **54**, 118 (1935).

thiazole.—A mixture of di-*p*-tolylthiourea (12.0g.), monochloroacetic acid (6.2 g.), anhydrous sodium acetate (6.0 g.) and absolute alcohol (45 cc.) was refluxed on a water-bath for 3 hours. The condensation was effected as above and the residual product was crystallised three times from absolute alcohol in cream colored feathery crystals (12.2 g.), m. p. 128° (Found : N, 9.49. Calcd. for $C_{17}H_{16}N_2OS$: N, 9.46%).

Semicarbazone.—A mixture of 2-*p*-tolylimino-3-*p*-tolyl-4-keto-tetrahydrothiazole (270 mg.), semicarbazide hydrochloride (300 mg.), anhydrous sodium acetate (500 mg.) and 95% alcohol (20 cc.) was refluxed for 15 minutes and then poured into water (60 cc.). The precipitate was crystallised two times from absolute alcohol in needles, m. p. 152° (Found: N, 19.78. Calcd. for $C_{18}H_{19}N_5OS$: N, 19.83%).

2-α-naphthylimino-3-α-naphthyl-4-keto-tetrahydrothiazole.—A mixture of di-α-naphthylthiourea (6.8 g.), monochloroacetic acid (3.0 g.), anhydrous sodium acetate (4.0 g.) and absolute alcohol (50 cc.) was heated on a steam-bath under reflux for 3 hours. The reaction was effected as above and the residue after washing free from acid was crystallised four times from absolute alcohol in grey leaflets (6.25 g.), m. p. 172–173° (Found : N, 7.63. Calcd. for $C_{23}H_{16}N_2OS$: N, 7.6%).

Semicarbazone.—The above compound (300mg.) was treated with 95% alcohol (20 cc.), semicarbazide hydrochloride (280 mg.) and anhydrous sodium acetate (450 mg.) and refluxed for 15 minutes. The mixture was poured into water (60 cc.) and the precipitate crystallised two times from absolute alcohol in leaflets, m. p. 186° (Found : N, 16.45. Calcd for $C_{24}H_{19}N_5OS$: N, 16.47%).

2-β-Naphthylimino-3-β-naphthyl-4-keto-tetrahydrothiazole.—Di-β-naphthylthiourea (7.0 g.) was suspended in absolute alcohol (50 cc.) and refluxed with monochloroacetic acid (3.0 g.) and finely powdered anhydrous sodium acetate (5.0 g.) for 3 hours on a steam-bath. The condensation was effected as above and the product after washing free from acid was crystallised three times from absolute alcohol in dark red needles (6.28 g.), m.p. 192–193° (Found : N, 7.56. Calcd. for $C_{23}H_{16}N_2OS$: N, 7.6%).

Semicarbazone.—A mixture of the above compound (320 mg.), 95% alcohol (20 cc.), semicarbazide hydrochloride (290 mg.) and finely powdered anhydrous sodium acetate (420 mg.) was refluxed for 15 minutes. The mixture was poured into water and the precipitate crystallised from absolute alcohol in brown needles, m. p. 208° (Found: N, 16.5. Calcd. for $C_{24}H_{19}N_5OS$: N, 16.47%).

2-*p*-Anisylimino-3-*p*-anisyl-4-keto-tetrahydrothiazole.—A suspension of di-*p*-anisylthiourea (5.5 g.) in absolute alcohol (40 cc) was treated with monochloroacetic acid (3.0 g.) and finely powdered anhydrous sodium acetate (4.0 g.) and refluxed for 3 hours on a steam-bath. The product after condensation was filtered rapidly while hot. The solvent was recovered by distillation and the residue crystallised three times from absolute alcohol in black needles (5.16 g.), m. p. 107–108° (Found: N, 8.56. Calcd. for $C_{17}H_{16}N_2O_3S$: N, 8.53%).

Semicarbazone.—The above compound (320mg.), 95% alcohol (20 cc.), semicarbazide hydrochloride (300 mg.) and finely powdered anhydrous sodium acetate (400 mg.) were refluxed for 20 minutes. The mixture was poured into water and the preciptate crystallised from absolute alcohol in dark brown needles, m. p. 120° (Found : N, 18.26. Calcd. for $C_{18}H_{19}N_5O_3S$: N, 18.18%).

2-*p*-Phenetylimino-3-*p*-phenetyl-4-keto-tetrahydrothiazole.—Di-*p*-phenetylthiourea (7.0 g.) was dissolved in absolute alcohol (50 cc.) and refluxed with monochloroacetic acid (3.0 g.) and anhydrous sodium acetate (4.0 g.) for 4 hours on a steam-bath. The resulting product after condensation was crystallised from absolute alcohol in brown needles (6.6 g.), m. p. 105–106° (Found : N, 7.84. Calcd. for $C_{19}H_{20}N_2O_3S$: N, 7.86%).

Semicarbazone.—A mixture of 2-*p*-phenetylimino-3-*p*-phenetyl-4-keto-tetrahydrothiazole (350 mg.) in 95% alcohol (22 cc.), semicarbazide hydrochloride (260 mg.) and finely powdered anhydrous sodium acetate (450 mg.) was refluxed on a steam-bath for 25 minutes. It was then poured into water and the precipitate crystallised from absolute alcohol in dark brown leaflets, m. p. 140° (Found: N, 16.98. Calcd. for $C_{26}H_{25}N_5O_3S$: N, 16.95%).

Summary

(1) 2-Arylimino-3-aryl-4-keto-tetrahydrothiazoles were prepared by condensation of di-arylthioureas with monochloroacetic acid in the presence of anhydrous sodium acetate and absolute alcohol.

(2) The formation of semicarbazones of 2-arylimino-3-aryl-4-keto-tetrahydrothiazoles has revealed the presence of a keto-group.

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